PHYSICAL REVIEW B VOLUME 16, NUMBER 12 15 DECEMBER 1977

Effect of controlled disorder on the electrical properties of TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane): High-temperature regime*

C. K. Chiang, Marshall J. Cohen, P. R. Newman, and A. J. Heeger
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104
(Received 27 May 1977)

The results of a study of the effects of controlled disorder on the electrical conductivity of the one-dimensional conductor, tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), are reported. We find that radiation-induced defects lead to effects which are relatively easy to establish from studies on a given set of crystals, and do not rely on subsequent synthesis and crystal growth. The temperature of the conductivity maximum increases with defect concentration [$dT_M/dc \simeq 5 \times 10^2$ K/(percent defects)], whereas the associated disorder suppresses the phase transitions to lower temperature. The first transition, associated with the onset of long-range order in pure TTF-TCNQ shifts downward with an initial slope of 1.5×10^2 K/(percent defects). The 38-K transition, associated with the final locking of the charge-density waves shifts to lower temperatures with an initial slope of 2×10^2 K/(percent defects). The data have been analyzed in the temperature range above the conductivity maximum to obtain quantitative information on the overall question of the importance of defects on the electrical transport properties of quasi-one-dimensional conductors. Both the conductivity peak ratio and the absolute magnitude of the room-temperature conductivity are extremely sensitive to induced defects at the level of 20 to 1000 ppm. The results are discussed in the context of the Peierls instability and the structural data available for the TTF-TCNQ system.

I. INTRODUCTION

Considerable effort has been devoted toward understanding the one-dimensional (1D) metallic behavior of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).[1] The observation[2,3] and detailed characterization[4-6] of the modulated superlattice structure at low temperatures has established the charge-density-wave (CDW) ground state associated with the Peierls instability, as proposed earlier based on experimental studies of dc,[7] microwave,[8] and optical electronic,[9] and magnetic properties.[10] The discovery of precursor phenomena[2-5,11] associated with the giant Kohn anomaly[12] and the divergent response functions expected for ideal 1D metals has made TTF-TCNQ a model system for experimental study.

In conjunction with these studies on pure single crystals of the parent compound, TTF-TCNQ, attempts have been made to create chemical isomorphs[13] and thereby enlarge the class of materials through synthetic means. The comparative studies on derivative salts with similar structural features and on alloys[14] (mixed systems such as $(TTF_x TSeF_{1-x})(TCNQ)$, where TSeF is tetraselenafulvalene) have been of importance in verifying the generality of the overall properties, while clearly pointing out differences in detailed behavior. However, the nature of the chemistry has set some limits on this approach. Alloys, for example, combine both the effects of structural disorder and different molecular electronic properties leading to results which are sometimes difficult to separate.

We report here the results of the first study, in quasi-1D conductors, of the effects of controlled disorder through radiation-induced defects.[15] Fast-particle bombardment is known as an effective method for controlled introduction of lattice defects into crystalline solids. In particular for organic 1D solids, we find that radiation-induced defects lead to cause-effect relationships which are direct and relatively easy to establish from studies on a given set of crystals, and do not rely on subsequent synthesis and crystal growth. The radiation induced defect studies therefore serve to explicitly quantify the importance of defects in nominally chemically "pure" crystals.

In this paper we report the effects of radiation damage on the dc electrical conductivity of single crystals of TTF-TCNQ in the metallic regime ($T > 54$ K). We include in addition an initial characterization of the corresponding effects in the region of the structural transitions ($30 < T < 55$ K). Detailed analysis of the effects of disorder on the phase transition will be discussed in the second paper in the series.[16] Related studies of microwave conductivity and dielectric constant and of the structural and magnetic properties are underway.

II. EXPERIMENTAL DETAILS

The TTF-TCNQ crystals used in this study were prepared in our laboratory. Crystals were grown by the diffusion method in acetonitrile

from multiply gradient sublimed TTF and TCNQ.[17] A specially designed diffusion cell was used in a programmable temperature controlled bath to produce quality single crystals. The electrical conductivity measurements were carried out using standard four-probe dc techniques on crystals taken at random from a single-crystal growth batch.

The radiation damage was carried out at the University of Pennsylvania Tandem linear accelerator using an 8-MeV deuteron beam. Optimum conditions resulted from placing the samples one at a time directly in the defocused beam. The 8-MeV deuteron beam current was in the range of 100 nA; total incident flux was determined with an integrating ammeter. Assuming the stopping power of TTF-TCNQ to be similar to that of amorphous carbon, crystals of TTF-TCNQ of typical thickness (50 μm) are essentially transparent to 8-MeV deuterons which lose less than 100 keV during passage. The experiments reported in this paper covered a total flux through the samples ranging from 10^{13} particles cm^{-2} to 5×10^{14} particles cm^{-2}.

In general the samples were irradiated and subsequently mounted for conductivity measurements after irradiation. However, several *in situ* measurements were carried out (see below) in which the room-temperature conductivity was monitored during the irradiation.

Only a small fraction of the deuteron energy loss in the sample results in defect production. Studies[18,19] of the low-temperature transport after irradiation at 5×10^{14} cm^{-2} indicate that the Ohmic conductance at 4.2 K was increased by more than two orders of magnitude, and was reproducible from sample to sample. This defect contribution is described[18,19] as $\sigma_d = \sigma_d^0 \exp(-E_d/k_BT)$ with $E_d/k_B = 20$ and $\sigma_d^0 \simeq 0.5\ (\Omega\,\mathrm{cm})^{-1}$. The single-characteristic activation energy suggests a single dominant defect. Spin-resonance studies[20] of the most heavily irradiated samples (flux 5×10^{14} cm^{-2}) indicate an induced concentration of spin-$\frac{1}{2}$ impurities of approximately 0.1% (1000 ppm). The measured value of $\sigma_d^0 \simeq 0.5\ (\Omega\,\mathrm{cm})^{-1}$ is consistent with 0.1% donor/acceptor states with a carrier mobility of order 2 cm^2/V sec consistent with that inferred from the room-temperature conductivity of TTF-TCNQ. Detailed studies of the resistivity in the temperature range 35–60 K show that for samples exposed to 5×10^{14} cm^{-2} of 8-MeV deuterons, the phase transitions, observed in pure samples as anomalies in the resistivity,[21] are suppressed. Similar experiments on alloys[14] indicate a comparable suppression of the phase transition at a level of about 3% TSeF in TTF-TCNQ. Because of the structural and electronic similarity of TSeF to TTF and the fact that the transitions are driven by the TCNQ chains,[22,23] we expect that for a given concentration the effect on the phase transitions of alloying to be somewhat less than that due to the irradiation-induced defects. It is difficult to establish definite error bars on this estimate of the total defect scale factor. The 0.1% concentration of magnetic defects (at a flux of 5×10^{14} cm^{-2}) is an approximate lower limit. An upper limit would be about 1% defects (at a flux of 5×10^{14} cm^{-2}) as inferred from the suppression of the transition temperatures. Based on the above arguments and the known result that chemical impurities play an important role at the 100-ppm level, we conclude that the value of 0.1% defects from an incident flux of 5×10^{14} cm^{-2} is approximately correct. We shall take this value to set the scale of the concentration of induced defects. Therefore, the experimental results described in this paper cover the range from approximately 20–1000 ppm.

III. EXPERIMENTAL RESULTS

Figure 1 shows the electrical conductivity of TTF-TCNQ after irradiation as a function of temperature near the conductivity maximum. The series of nested curves (each one normalized to the room-temperature value measured for that crystal) result from progressively higher flux or equivalently progressively higher defect concentration. The characteristic behavior of TTF-TCNQ has not changed due to the irradiation; the electrical conductivity increases with decreasing temperature, goes through a relatively sharp maximum at a temperature T_M and becomes activated (a semiconductor) at low temperatures.

The phase transitions, observed in pure TTF-TCNQ in the temperature range 35–54 K, remain observable for the irradiated samples. However, the transitions broaden and shift to lower temperature with increasing defect concentration. Figure 2 shows the resistivity in the transition region of several samples with progressively higher defect concentrations. The detailed behavior and analysis of the results in the vicinity of the phase transitions will be presented in a subsequent paper.[16] For the purpose of the present discussion we note only the dependence of the transition temperatures (defined by the peak in $d\ln\rho/dT$) as a function of defect concentration.

The results for the three characteristic temperatures are shown in Fig. 3.

(a) T_M: The temperature of the conductivity maximum occurs at 58 K in pure TTF-TCNQ and *increases* to 68 K at a defect level of 1000

ppm. Note that samples with conductivity maximum at 60 K have of order 50 ppm added defects.

(b) T_1: The first transition, associated with the onset of long-range order in pure TTF-TCNQ, shifts to lower temperatures. The effect of disorder is to suppress the phase transition from 52.3 K in our pure samples downward with an initial slope $dT_1/dc \simeq 150$ K/(percent defects).

(c) T_2: The 38-K transition, associated with the final locking of the CDW's on the two chains in pure TTF-TCNQ also shifts to lower temperatures; $dT_2/dc \simeq 200$ K/(percent defects).

There has been considerable controversy concerning the dc electrical conductivity[24-27] of TTF-TCNQ centering on the absolute magnitude of the

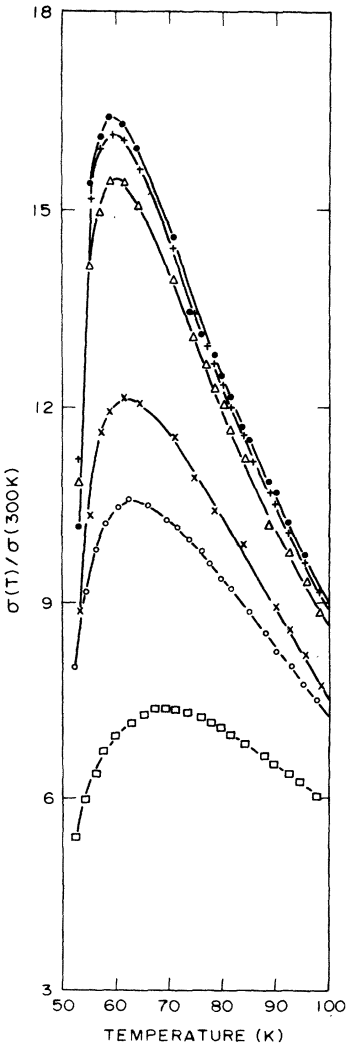

FIG. 1. Electrical conductivity of TTF-TCNQ after irradiation as a function of temperature near the conductivity maximum. ●, nonirradiated; +, 1.1×10^{13} cm^{-2}; Δ, 2.4×10^{13} cm^{-2}; ×, 5.2×10^{13} cm^{-2}; ○, 9.3×10^{13} cm^{-2}; □, 51.5×10^{13} cm^{-2}.

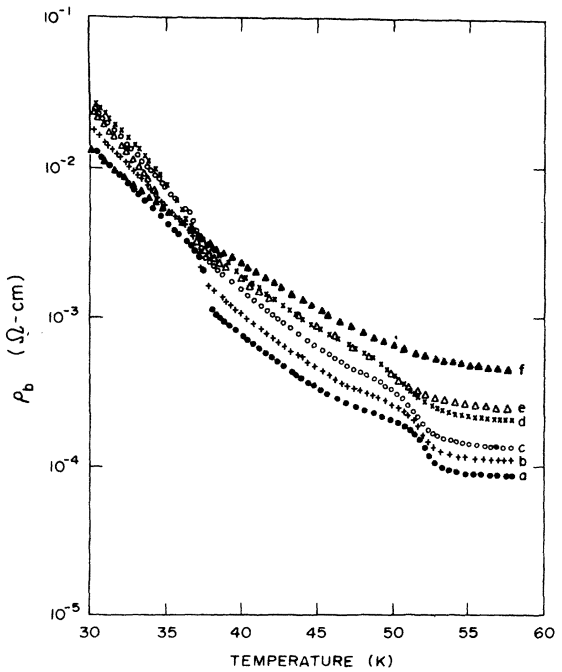

FIG. 2. Resistivity in the transition region from several samples with progressively higher defect concentration. (a) ●, nonirradiated; (b) +, 1.1×10^{13} cm^{-2}; (c) ○, 2.4×10^{13} cm^{-2}; (d) ×, 5.2×10^{13} cm^{-2}; (e) Δ, 9.3×10^{13} cm^{-2}; (f) ▲, 51.5×10^{13} cm^{-2}.

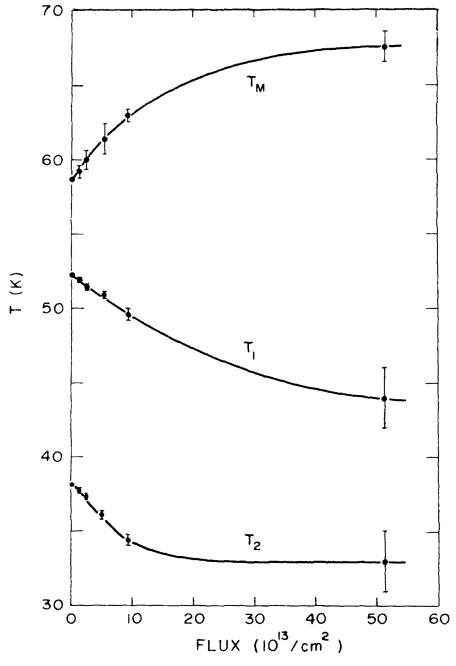

FIG. 3. Characteristic temperatures of TTF-TCNQ as a function of incident flux or defect concentration; T_M is the temperature of the conductivity maximum, T_1 is the first transition associated with the onset of long-range order in pure TTF-TCNQ, and T_2 is the 38-K transition associated with the locking of CDW's.

room-temperature conductivity, the size of the conductivity peak ratio (CPR)[$\equiv\sigma(T_M)/\sigma(300\ \mathrm{K})$] and the temperature at which the peak occurs (T_M). Our results for T_M are shown in Fig. 3; our results on the absolute magnitude of $\sigma(300\ \mathrm{K})$ and for the CPR are shown in Figs. 4 and 5.

Figure 4 shows the room-temperature conductivity, $\sigma(300\ \mathrm{K})$, of TTF-TCNQ as a function of particle flux. The solid line represents the experimentally determined variation of the conductivity obtained by on-line measurements. A sample was mounted for four-probe conductivity measurements and placed in the scattering chamber; the voltage and current were remotely monitored at short intervals (beam off) during the irradiation. The experimental points were obtained from samples irradiated as described in Sec. II and subsequently measured. The agreement and reproducibility are remarkable and satisfying. Moreover the extreme sensitivity of the room-temperature conductivity to defects is clearly evident. The room-temperature conductivity values reported by other laboratories typically fall in the region from 300 to 500 $(\Omega\,\mathrm{cm})^{-1}$.[25] Figure 4 demonstrates that such values are characteristic of defect levels in excess of about 100 to 200 ppm. Thus the correlation suggested earlier[7,26,27] between the room-temperature conductivity and increased sample quality is verified by the present studies.

The conductivity peak ratio $\sigma(T_M)/\sigma(300\ \mathrm{K})$ is plotted as a function of particle flux in Fig. 5. As long as the CPR is much greater than 2, this quantity will be an approximate indicator of sample quality; in effect a measure of the residual resistivity if interpreted in the conventional metallic sense. With the starting samples having only moderate quality (CPR of the order

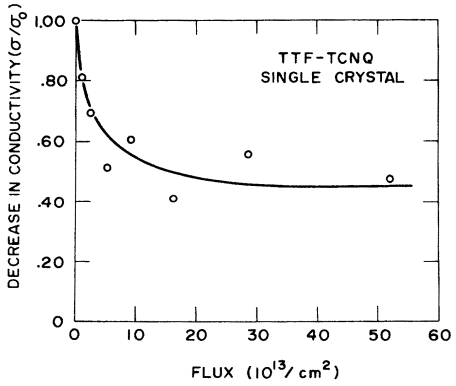

FIG. 4. Room-temperature conductivity, $\sigma(300\ \mathrm{K})$, as a function of particle flux and defect concentration. The solid curve represents on-line measurements of a single sample; the experimental points are from separate samples measured subsequently (see text).

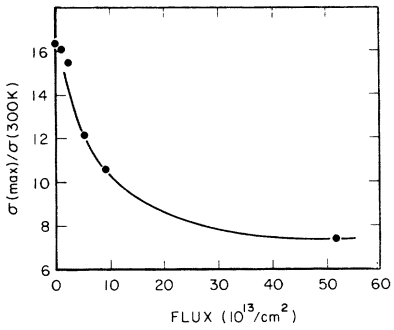

FIG. 5. Conductivity peak ratio as a function of particle flux and defect concentration.

of 16), we are unable to extrapolate back to predict the CPR of the purest defect free TTF-TCNQ. However, by observing the defect concentration needed to reduce the CPR by a factor of 2 we can evaluate the approximate defect and/or impurity level in nominally-high-purity TTF-TCNQ; i.e., characterized by $\sigma(300\ \mathrm{K}) \simeq 700\ (\Omega\,\mathrm{cm})^{-1}$ and CPR$\simeq$16–20 (typically). Figure 4 quantitatively characterizes such samples as having of order 100-ppm defects and/or impurities.

IV. ANALYSIS OF EXPERIMENTAL RESULTS

The temperature dependence of the electrical resistivity of TTF-TCNQ in the high-temperature conducting regime was discussed by Groff *et al.*[28] Taking the point of view of simple metallic behavior, the resistivity is separated into a temperature-dependent intrinsic term and a temperature-independent residual term, i.e.,

$$\rho(T) = \rho_0 + \rho_1 (T/T_0)^{\lambda}. \tag{1}$$

Equation (1) assumes a simple power law for the intrinsic temperature dependence. Underlying Eq. (1) is the assumption that ρ_0 will be proportional to the defect concentration, whereas the power λ and the coefficient $A = \rho_1 T_0^{-\lambda}$ are assumed to be intrinsic and therefore independent of defects at least in the low-concentration limit.

In an attempt to evaluate the validity of Eq. (1), we have carried out least-squares fits to our data. To avoid a preference for either conductivity or resistivity, the following was minimized:

$$\chi^2 \equiv \sum_i \left(\frac{y_i - y_{\mathrm{cal}}}{y_i}\right)^2, \tag{2}$$

where y_i denotes the data point at a temperature T and y_{cal} is the calculated value from Eq. (1). For each λ, $x \equiv T^{\lambda}$ was defined so that

$\rho_{cal} = \rho_0 + A\lambda$ and the matrix equation $\partial\chi^2/\partial\rho_0 = 0$, $\partial\chi^2/\partial A = 0$ was inverted to find the best ρ_0 and A. The power λ was incremented to find the absolute minimum in χ^2. For a given set of data (over a given temperature range), λ, ρ_0, and A are the best parameters that describe the data. For a given temperature range the only error comes from the scatter in the data. The variance in λ was calculated using the formula

$$\Delta\lambda = \left[\sum_i \left(\frac{\partial\lambda}{\partial y_i}\Delta y_i\right)^2\right]^{1/2}, \tag{3}$$

where Δy_i is the error in an individual datum point. For an (overestimated) scatter of $\Delta y/y \simeq 2\%$, we find $\Delta\lambda = 0.035$.

Figure 6 represents a test of the validity of Eq. (1). For a typical nondamaged sample, we have carried out the fitting procedure described above over a temperature interval $T_F < T < 300$ K. We plot the resulting λ_F as a function of T_F. If Eq. (1) were a true description of the data, the same λ_F would be found for any temperature interval; i.e., λ_F would be independent of T_F. The results show λ_F varying significantly; the error bar indicates the variance, $\Delta\lambda$, as calculated above assuming 2% scatter in the data. The value of λ_F approaches $\lambda = 2.3$ when the fit includes the entire temperature interval $80 < T < 300$ K in agreement with the results of Groff *et al.*[27] who found $\lambda = 2.33 \pm 0.14$. However, the strong dependence of λ_F on T_F indicates that Eq. (1) is only a rough approximation and should not be taken to have fundamental physical significance. The true temperature dependence is more complex involving at least higher terms and possibly an altogether different functional form. Nevertheless, with this caveat in mind, we find it useful to categorize and quantify the effects of induced defects in terms of the parameters of Eq. (2).

We have carried out least-squares fits of our data to Eq. (1) for irradiated samples over the full range of induced-defect concentrations. The

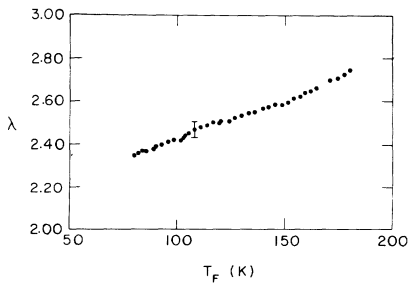

FIG. 6. Power-law parameter λ as a function of T_F where the fitting parameters were determined from data from successive intervals $T_F < T < 300$ K.

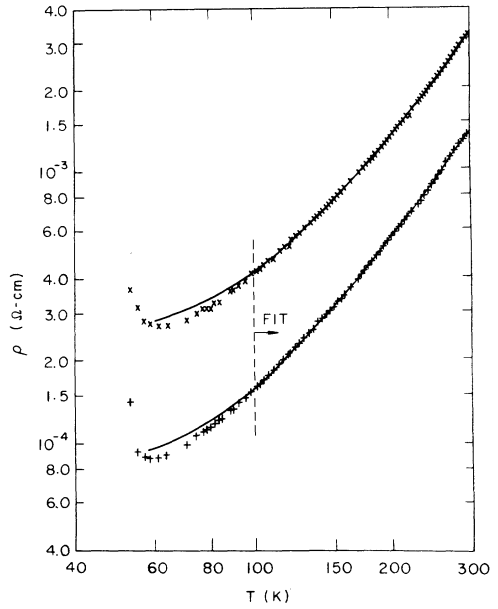

FIG. 7. Examples of best fit (solid line) of Eq. (1) to two samples; the lower-resistivity sample was not irradiated, the higher-resistivity sample was exposed to a total flux of 2.8×10^{14} cm^{-2}.

results are shown in Figs. 7–9. Figure 7 shows the best fit to two samples; one not irradiated and the second exposed to a total flux of 2.8×10^{13} cm^{-2}. The data are plotted as $\ln\rho$ vs $\ln T$ to show clearly the entire range. Absolute values of ρ are given for the two samples. As indicated above, the resistivity increases on irradiation. The overall temperature dependence for both samples is in agreement with Eq. (1) as indicated by the solid curves which represent best fits (input data for fitting restricted to the region above 100 K). As expected, ρ_0 increases with induced defects. However, our analysis shows that over the defect range studied, no significant change in λ could be detected. The fits to the experimental data set an

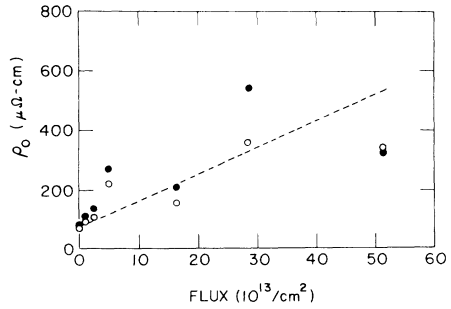

FIG. 8. Residual resistivity ρ_0 as a function of particle flux and defect concentration. The open circles result from fitting the data to Eq. (1); the solid points correspond to the measured minimum resistivity (at T_M).

upper limit of $\Delta\lambda/\lambda < 0.02$ which is within the uncertainty as described above; see Fig. 6.

Figure 8 shows the residual resistivity ρ_0 as a function of flux. The results indicate that

$$\rho_0 = \alpha c, \tag{4}$$

where c is the defect concentration and $\alpha \simeq 5\times10^{-3}$ (Ω cm)/%. The extreme sensitivity of the quasi-one-dimensional system to defects is evident. Figure 9 shows the coefficient $A = \rho_1 T_0^{-\lambda}$ [see Eq. (1)] as a function of flux. Note that both the values for ρ_0 (Fig. 7) and A (Fig. 9) are dependent on the careful determination of sample dimensions and require stringent reproducibility for different samples. The data obtained in this study meet this standard as evidenced by the excellent agreement between the on-line data and the room-temperature results from different samples shown in Fig. 3. The normalized on-line data are replotted in Fig. 9 as confirmation of the dependence of the prefactor $A = \rho_1 T_0^{-\lambda}$ on defect concentration. The strong dependence of the coefficient A on defect concentration is unexpected and represents an unusual breakdown of Matthiessen's rule. The sensitivity of the "intrinsic" temperature-dependent term to defects is not an artifact of the data analysis; the results plotted in Fig. 9 can be anticipated by direct examination of the room-temperature data in Fig. 3. The initial decrease in σ(300 K) followed by saturation at higher flux levels is the direct result of the change in the temperature-dependent term. Note that the variation of CPR (Fig. 4) and ρ_0 (Fig. 8) as a function of particle flux provides additional evidence that the defect concentration is proportional to the particle flux over the entire range under study.

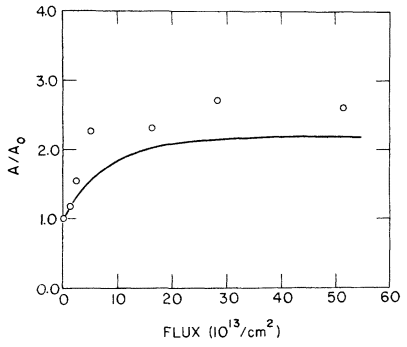

FIG. 9. Prefactor $A = \rho_1 T_0^{-\lambda}$ from Eq. (1) as a function of particle flux and defect concentration (the initial value is $A_0 += 1.1\times10^{-8}$). The solid curve is the normalized on-line room-temperature data from Fig. 4.

V. DISCUSSION

Any discussion of the mechanism and temperature dependence of the electrical conductivity in the "metallic" regime must take into account the known structural aspects[2-5,11] of the problem. The observation[2-5] of strong 1D x-ray scattering at $2k_F$ ($0.295b^*$) and $4k_F$ ($0.59b^*$ or equivalently $0.41b^*$) at temperatures above 54 K indicate precursor structural fluctuations associated with the CDW state established at lower temperatures. The $2k_F$ anomaly has been identified through inelastic-neutron-scattering studies[11] as originating from a soft mode in the phonon spectrum due to the giant Kohn anomaly associated with the divergent $2k_F$ response of the 1D electron system. The detailed origin of the $4k_F$ anomaly remains under study. The major structural features are, therefore, the observation of the incommensurate charge-density-wave ground state, the transitional region between 38 and 54 K, and the observation of 1D precursor effects associated with the giant Kohn anomaly above 54 K. Correlations between chains increase (in pure TTF-TCNQ) in the temperature interval $54 < T < 60$ K, where the results of Khanna *et al.*[6] show the 1D streaks coalescing into Bragg spots with the onset of transverse order. In the conducting regime, above 58 K, the dynamical distortion has a well-defined periodicity ($\lambda_s = 3.4b$) and a relatively long temperature-dependent coherence length. The x-ray observations indicate stronger scattering as the temperature is lowered with an apparent divergence as $T \to 54$ K.

The lifetime of a $2k_F$ dynamical distortion will be relatively long on the scale of electronic times; certainly greater than $1/\omega_{ph}$ so that the electrons will experience a periodic superlattice potential ($\lambda_s = 3.4b$) over a distance $\Lambda \gtrsim v_F/\omega_{ph} \gtrsim 100$ Å. Therefore, just as the x rays scatter from the finite coherence-length dynamical distortion, so, too, would the electronic Bloch waves scatter as a result of the electron-phonon interaction. Thus the *increasing $2k_F$ x-ray scattering* with decreasing temperature would directly imply a corresponding *increase in electron $2k_F$ back scattering* across the Fermi surface with a reduction in the electron transport mobility and the formation of a pseudogap in the electronic density of states. The x-ray data for $58 < T < 150$ K lead to the conclusion that the single-particle contribution to the electrical conductivity decreases as the temperature is lowered.

The principal experimental results obtained in the present study relevant to the question of single particle versus collective transport are the dependence of the peak temperature (T_M) and the transition temperatures (T_1 and T_2) on defect con-

centration (Fig. 3); and the effect of radiation-induced defects on the CPR (Fig. 5) and the phenomenological parameters ρ_0, A, and λ (Figs. 7, 8, and 9).

The observed increase in T_M with defect concentration can be understood in terms of a fluctuation CDW collective transport mechanism.[29-32] The relatively long coherence-length CDW fluctuations would be expected to exhibit local random pinning of the phase in the presence of defects and impurities as shown by Lee, Rice, and Anderson,[33] Fukuyama, Rice, and Varma,[34] and Gorkov.[35] Qualitatively, we would also anticipate a rounding of the peak since the defect pinning is random and unrelated in detail to the buildup of transverse phase coherence. Moreover, the effect of defects would be to suppress[36] the onset of long-range order, as observed experimentally.

The opposite dependence of T_M and T_1 on defect concentration is difficult to understand on the basis of single-particle theory in which the decrease in conductivity just above the phase transition is usually attributed to the onset of transverse coherence and the associated formation of an energy gap. The experimental results indicate a suppression of long-range order (and by implication a suppression of the onset of a mean-field gap) to lower temperatures while T_M increases.

Alternatively, the decrease in CPR and the shift in T_M toward higher temperatures would be expected from 1D localization of the single-particle electronic wave functions due to the induced disorder. Bychkov,[37] Berezinsky,[38] and Gogolin, Mel'nikov, and Rashba[39] have shown that for independent electrons in a 1D system containing defects or impurities, the conductivity should decrease as the temperature is lowered approaching zero with a temperature dependence determined by the ratio of the impurity and phonon-scattering rates $\tau_{\text{imp}}/\tau_{\text{ph}}(T)$. Within this theory, the conductivity will increase with decreasing temperature until $\tau_{\text{ph}}(T) > \tau_{\text{imp}}$ at which point the defect localization will dominate. The experimental results for $\sigma_{(T)}$ in the irradiated samples are in qualitative agreement with such predictions.

The effect of induced defects on the temperature dependence of the conductivity can be discussed in terms of the parameters ρ_0, A, and λ of Eq. (1). The approximately linear dependence of $\rho_0(c)$ is expected and simply provides some indication of the importance of defects as scattering centers. For example $\rho_0 = \alpha c$ with $\alpha \simeq 5\times10^{-3}$ (Ω cm)/(% defects) is in magnitude consistent with defects blocking a given chain causing interchain ($\rho_\perp$) series resistance to play an important role. Since $\rho_\perp$ is only weakly temperature dependent[7,8] above 58 K, such an effect would appear as an apparent residual resistivity.

The T^λ dependence has been interpreted as resulting from single-particle transport dominated by electron-electron scattering.[41] However, the dependence as observed experimentally appears to be stronger than T^2. Moreover, the traditional T^2 power-law dependence associated with electron-electron scattering in three-dimensional systems is not expected in a 1D system. For 1D metals electron-electron scattering resistivity should be linear in T; the Fermi surface is a point so that angular scattering around the Fermi surface is forbidden, and the traditional second factor of k_BT/E_F does not appear.[42]

The theoretical understanding of the sliding mode dc conductivity, $\sigma_F(T)$, within the Peierls-Fröhlich model has developed slowly since the original suggestion by Bardeen.[30] Patton and Sham argued initially that the Fröhlich state was pararesistive[43] and later obtained results indicating $\sigma_F = \infty$.[44] Allender, Bray, and Bardeen[31] developed a phenomenological theory for the initial fluctuation regime at high temperature. Their results were derived microscopically by Strassler and Tombs.[45] Rice[46] has calculated the dc electron-hole relaxation rate $1/\tau$ leading to an estimate of the Fröhlich conductivity through the relation

$$\sigma_F = N_s e^2 \tau / M^*, \tag{5}$$

where M^* is the Fröhlich charge-density-wave effective mass. Since the theory neglects anharmonic elastic effects, the resulting value of σ_F represents an apparent upper limit to the sliding mode conductivity. The resulting electron-hole relaxation rate is given by

$$1/\tau = \lim_{\omega\to 0} (\pi/2\omega)\,\lambda\omega_0^2[N(\tfrac{1}{2}\omega)/N_0]\tanh(\omega/4k_BT), \tag{6}$$

where λ is the electron-phonon coupling constant, ω_0 is the bare phonon frequency, N_0 is the unperturbed electronic density of states at the Fermi energy, and $N(\frac{1}{2}\omega)$ is the actual electronic density of states in the 1D fluctuation regime at frequency $\frac{1}{2}\omega$. Using the Lee-Rice-Anderson theory[33] for the density of states in the fluctuation regime, one obtains[46]

$$\sigma_F = \frac{Ne^2}{m^*}\left(\frac{N_s}{N}\right)^2\left(\frac{4k_BT}{\pi\Delta}\right)\frac{\xi(T)}{v_F}, \tag{7}$$

where m^* is the band mass, $2\Delta = E_g$ is the energy gap, $\xi(T)$ is the order parameter coherence length, v_F is the unperturbed Fermi velocity, and

N_s is the number of electrons in the condensed state. For temperatures well below the mean-field Peierls temperature T_P^{MF} the order parameter and energy gap are well formed and $N_s/N \simeq 1$. The existence of the optical energy gap[9] at temperatures in the "metallic" regime provides evidence that this is the case in TTF-TCNQ at least below 150 K. In this case

$$\sigma_F = \sigma_0(4k_BT/\pi\Delta)[\xi(T)/b] , \tag{8}$$

where $\sigma_0 = (Ne^2/m^*)(b/v_F) \simeq 500$ to $1000\ (\Omega\,\mathrm{cm})^{-1}$ using values appropriate to TTF-TCNQ. The implied temperature dependence reflects the growth of the coherence length $\xi(T)$ for which experimental data are available from the diffuse x-ray scattering studies of Khanna *et al.*[6] Comparison of Eq. (8) with the T^λ dependence inferred from the conductivity measurements implies $\xi(T)/b \sim T^{-(\lambda+1)}$. We replot the results of Khanna *et al.*[6] in Fig. 10. The observed temperature dependence of the coherence length is consistent with a power-law dependence with $\lambda \simeq 2.3$ in satisfactory agreement with the transport results.

The breakdown of Matthiessen's rule reflected in the rapid change in room-temperature resistivity (Fig. 3) and in the coefficient $A = \rho_1 T_0^{-\lambda}$ with irradiation is a surprising result. Such an effect is difficult to understand from single-particle theory where the different scattering mechanisms would not interfere. From the point of view of Eq. (5), the change in A is attributed either to a change in the effective oscillator strength (Ne^2/M^*) or to a reduction in mean-field scale temperature and an associated decrease in the coherence length [Eq. (8)]. Although both the Fröhlich effective mass and the scale temperature might be sensitive to impurity or defect concentration, we currently have no detailed theoretical understanding of this result.

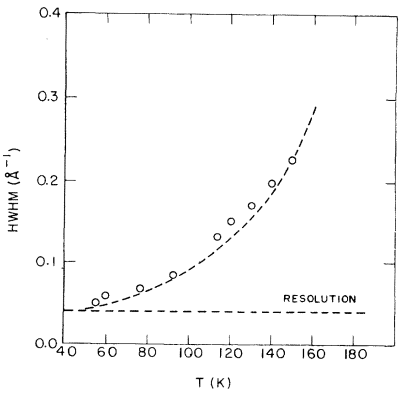

FIG. 10. Half-width at half-maximum (HWHM) of the $2k_F$ streak as a function of temperature (from Khanna *et al.*, Ref. 6). The dashed curve represents a $T^{\lambda+1}$ dependence as suggested by Eqs. (1) and (8).

VI. SUMMARY AND CONCLUSION

In this paper we have presented the results of an experimental study of the effect of irradiation induced defects on the electrical conductivity of TTF-TCNQ with emphasis on the high-temperature "metallic" regime. The results have been analyzed to obtain quantitative information on the overall question of the importance of defects on the transport properties of quasi-one-dimensional conductors.

The principal results are as follows: (i) The conductivity peak ratio decreases with increasing defect concentration (Figs. 1 and 5). (ii) The temperature of the conductivity peak (T_M) increases with increasing irradiation while the associated disorder suppresses the onset of long-range order to lower temperatures (Fig. 3). (iii) Detailed analysis of the conductivity as a function of temperature and defect concentration (Figs. 7, 8, and 9) provides information relevant to the determination of the mechanism for transport.

The transport results are discussed in the context of the known structural aspects of the problem. It is shown that the observed magnitude and temperature dependence are consistent with the growth of long coherence-length CDW fluctuations which contribute to the conductivity particularly in the temperature range below 150 K where there is independent evidence of such long coherence-length CDW fluctuations from diffuse x-ray scattering measurements. Related studies of the microwave conductivity and dielectric constant and of the structural and magnetic properties of irradiated TTF-TCNQ are underway and should provide additional information toward the eventual understanding of the electrical transport in this prototype one-dimensional organic metal.

ACKNOWLEDGMENTS

We thank Professor R. Zurmuhle and L. Mulligan and the Tandem Laboratory at the University of Pennsylvania for help and assistance. Without their help and cooperation, the irradiation experiments could not have been done. We are grateful to Y. W. Park for help with the data reduction. The high-quality crystals used in this study were grown by Paul Nigrey.

*Work supported by the Army Research Office through Contract No. DAAG29-77-G-0089.

[1]*Low Dimensional Cooperative Phenomena*, edited by H. J. Keller (Plenum, New York, 1975); *Lecture Notes in Physics: One-Dimensional Conductors* (Springer, New York, 1975), Vol. 34; A. J. Berlinsky, Contemp. Phys. 17, 331 (1976); J. J. Andre, A. Bieber, and F. Gautier, Ann. Phys. (Leipz.) 1, 145 (1976); *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. Keller (Plenum, New York, 1977).

[2]F. Denoyer, R. Comés, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 445 (1975).

[3]S. Kagoshima, H. Anzai, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn. 39, 1143 (1975).

[4]R. Comés, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 35, 1518 (1975); R. Comés, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. B 14, 2376 (1976).

[5]S. Kagoshima, T. Ishiguro, and H. Anzai, J. Phys. Soc. Jpn. 41, 2061 (1976).

[6]J. P. Pouget, S. K. Khanna, F. Denoyer, R. Comés, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 37, 437 (1976); S. K. Khanna, J. P. Pouget, R. Comés, A. F. Garito, and A. J. Heeger, Phys. Rev. B 16, 1468 (1977).

[7]M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1298 (1974); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, Solid State Commun. 12, 1125 (1973).

[8]S. K. Khanna, E. Ehrenfreund, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 2205 (1974); M. Cohen, S. K. Khanna, W. J. Gunning, A. F. Garito, and A. J. Heeger, Solid State Commun. 17, 367 (1975); S. K. Khanna, A. F. Garito, A. J. Heeger, and R. C. Jaklevic, *ibid*. 16, 667 (1975).

[9]A. A. Bright, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1328 (1974); D. B. Tanner, C. S. Jacobsen, A. F. Garito, and A. J. Heeger, *ibid*. 13, 3381 (1976).

[10]J. C. Scott, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 3131 (1974).

[11]G. Shirane, S. M. Shapiro, R. Comés, A. F. Garito, and A. J. Heeger, Phys. Rev. B 14, 2325 (1976).

[12]A. M. Afanas'ev and Yu. Kagan, Zh. Eksp. Teor. Fiz. 43, 1456 (1963) [Sov. Phys.-JETP 16, 1030 (1963)].

[13]An entire class of salts has been made using derivatives of the TTF molecule. Examples are TSeF (tetraselenafulvalene), ATTF (di-methyl-TTF), TMTTF (tetramethyl-TTF), HMTTF (hexamethylene-TTF), HMTSeF (hexamethylene-TSeF), etc. For detailed references, see *Chemistry and Physics of One-Dimensional Metals*, edited by H. J. Keller (Plenum, New York, 1975).

[14]Y. Tomkiewicz, A. R. Taranko, and E. M. Engler, Phys. Rev. Lett. 37, 1705 (1976); see also, S. Etemad, Phys. Rev. B 13, 2254 (1976).

[15]A preliminary version of this work was presented at the Meeting of the American Physical Society, March, 1977, San Diego, Calif.; see C. K. Chiang, M. J. Cohen, P. R. Newman, Y. W. Park, and A. J. Heeger, Bull. Am. Phys. Soc. 22, 395 (1977).

[16]C. K. Chiang, Y. W. Park, and A. J. Heeger (unpublished).

[17]See Ref. 8 for a description of the materials purification.

[18]Marshall J. Cohen, P. R. Newman, and A. J. Heeger, Phys. Rev. Lett. 37, 1500 (1976).

[19]Marshall J. Cohen and A. J. Heeger, Phys. Rev. B 16, 688 (1977).

[20]P. R. Newman and L. S. Smith (private communication).

[21]D. Jerome, W. Muller, and M. Weger, J. Phys. Lett. (Paris) 35, L77 (1974); S. Etemad, Phys. Rev. B 13, 2254 (1976); P. Horn and D. Rimai, Phys. Rev. Lett. 36, 809 (1976); T. Ishiguro, S. Kagoshima, H. Anzai, J. Phys. Soc. Jpn. 41, 351 (1976).

[22]Y. Tomkiewicz, A. Taranko, and J. B. Torrance, Phys. Rev. Lett. 36, 751 (1976); Y. Tomkiewicz, R. A. Craven, T. D. Schultz, E. M. Engler, and A. R. Taranko, Phys. Rev. B (to be published).

[23]E. F. Rybaczewski, L. S. Smith, A. F. Garito, A. J. Heeger, and B. G. Silbernagel, Phys. Rev. B 14, 2746 (1976).

[24]D. E. Schafer, F. Wudl, G. A. Thomas, J. P. Ferraris, and D. O. Cowan, Solid State Commun. 14, 347 (1974).

[25]G. A. Thomas, D. E. Schafer, F. Wudl, P. M. Horn, D. Rimai, J. W. Cook, D. A. Glocker, M. J. Skove, C. W. Chu, R. P. Groff, J. L. Gillson, R. C. Wheland, L. R. Melby, M. B. Salamon, R. A. Craven, G. De Pasquali, A. N. Bloch, D. O. Cowan, V. V. Walatka, R. E. Pyle, R. Gemmer, T. O. Poehler, G. R. Johnson, M. G. Miles, J. D. Wilson, J. P. Ferraris, T. F. Finnegan, R. J. Warmack, V. F. Raaen, and D. Jerome, Phys. Rev. B 13, 5105 (1976).

[26]Marshall J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B 13, 5111 (1976).

[27]Marshall J. Cohen, thesis (University of Pennsylvania, 1975) (unpublished); L. B. Coleman, thesis (University of Pennsylvania, 1975) (unpublished).

[28]R. Groff, A. Suna, and R. Merrifield, Phys. Rev. Lett. 33, 418 (1974).

[29]H. Fröhlich, Proc. R. Soc. A 223, 296 (1954).

[30]J. Bardeen, Solid State Commun. 13, 357 (1973).

[31]D. Allender, J. W. Bray, and J. Bardeen, Phys. Rev. B 9, 119 (1974).

[32]M. J. Rice, in *Low Dimensional Cooperative Phenomena*, edited by H. J. Keller (Plenum, New York, 1975), p. 23.

[33]P. A. Lee, T. M. Rice, and P. W. Anderson, Solid State Commun. 14, 703 (1974). See also, M. J. Rice and S. Strässler, Solid State Commun. 13, 1389 (1973).

[34]H. Fukuyama, T. M. Rice, and C. M. Varma, Phys. Rev. Lett. 33, 305 (1974).

[35]L. Gorkov, Solid State Commun. (to be published).

[36]Y. Imry and S. Ma, Phys. Rev. Lett. 35, 1399 (1975).

[37]Y. A. Bychkov, Zh. Eksp. Teor. Fiz. 65, 427 (1973) [Sov. Phys.-JETP 38, 209 (1974)].

[38]V. L. Berezinskii, Zh. Eksp. Teor. Fiz. 65, 1251 (1973) [Sov. Phys.-JETP 38, 620 (1974)].

[39]A. A. Gogolin, V. I. Mel'nikov, and E. I. Rashba, Zh. Eskp. Teor. Fiz. 69, 327 (1975) [Sov. Phys.-JETP 42, 168 (1976)].

[40]A. A. Gozolin, S. P. Zolotukhim, V. I. Mel'nikov, E. I. Rashba, and I. F. Shchegolev, Zh. Eksp. Teor. Fiz. Pis'ma Red. 22, 564 (1975) [JETP Lett. 22, 278 (1975)].

[41]P. E. Seiden and D. Cabib, Phys. Rev. B 13, 1846 (1976).

[42]We thank Dr. L. P. Gorkov for pointing this out to us; see L. P. Gorkov and I. E. Dzialoshinskii, Zh. Eksp. Toer. Fiz. Pis'ma, Red. 18, 686 (1975) [JETP Lett.

18, 401 (1973)].
[43]B. R. Patton and L. J. Sham, Phys. Rev. Lett. 31, 631 (1973).
[44]B. R. Patton and L. J. Sham, Phys. Rev. Lett. 33, 638 (1974).
[45]S. Strässler and G. A. Toombs, Phys. Lett. A 46, 321 (1974).
[46]M. J. Rice, Solid State Commun. 16, 1285 (1975).