Temperature Dependence of the Near-Infrared Optical Properties of Tetrathiofulvalinium Tetracyanoquinodimethane (TTF-TCNQ)

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(Received 13 August 1973)

We report the near-normal-incidence reflectivity spectrum of single-crystal TTF-TCNQ in the range 0.2–2.0 μm. A Drude-like edge, persisting through the metal-insulator transition at 60°K, is observed near 1.3 μm for light polarized parallel to the conducting axis. The temperature dependence of the optical parameters ϵ_0, τ, and ω_p are discussed in conjunction with Hopfield's relation for the electron-phonon coupling constant.

Two groups have recently reported observing high dc[1,2] and microwave[3] conductivity at room temperature in the organic charge-transfer salt tetrathiofulvalinium tetracyanoquinodimethane (TTF-TCNQ). Furthermore, the conductivity increases with decreasing temperature to approximately $10^4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ before the onset of a metal-insulator (MI) transition at ~60°K. In a few TTF-TCNQ crystals, one group[2] measured a dc conductivity in excess of $10^6\ \Omega^{-1}\ \mathrm{cm}^{-1}$ slightly preceding the transition and attributed this unusually high value to the onset of superconducting fluctuations. Both groups point out that the MI transition possibly arises from a Peierls distortion which introduces a gap in the electronic band structure.[4] It is felt that the electron-phonon interaction plays a crucial role in these phenomena, and several theoretical papers have discussed its implications for the high conductivity and the Peierls instability.[5]

We report here the first measurements[6] of the polarized reflectance of TTF-TCNQ single crystals covering the entire wavelength region 0.2–2 μm (0.6–4.5 eV) and at temperatures both above and below the MI transition (20–300°K). Independent measurements,[7] similar to ours, have been made above the transition in the region 1.0–2.5 μm. The most significant feature of our data is a metalliclike plasma edge whose character does not change appreciably through the MI transition. This result is consistent with both the interpretation of TTF-TCNQ as a metal above 60°K and the assertion that any gap opened up in the electronic spectrum below 60°K is small. In addition, we find that the optical conductivity has a significantly different temperature dependence than the dc conductivity over the range $60 < T < 300$°K. This suggest that processes other than the electron-phonon interaction dominate the optical relaxation. The data presented here will also be germane to the eventual understanding of the band structure of this unusual class of materials.

The single-crystal samples were in the form of $5\times1\times0.05\ \mathrm{mm}^3$ platelets grown by slow cooling from an acetonitrile solution. These samples exhibited the "typical" conductivity behavior observed by most other workers, that is, a room temperature $\sigma \sim 200$–$600\ \Omega^{-1}\ \mathrm{cm}^{-1}$, $\sigma(60°\mathrm{K})/\sigma_{\mathrm{RT}} \sim 10$–$15$. Details of the experimental methods and the sample preparation will be discussed elsewhere.

The crystal structure of TTF-TCNQ[8] is similar to other conducting TCNQ salts; hence we expect, and indeed observe, anisotropic electrical and optical properties. Figure 1 gives the

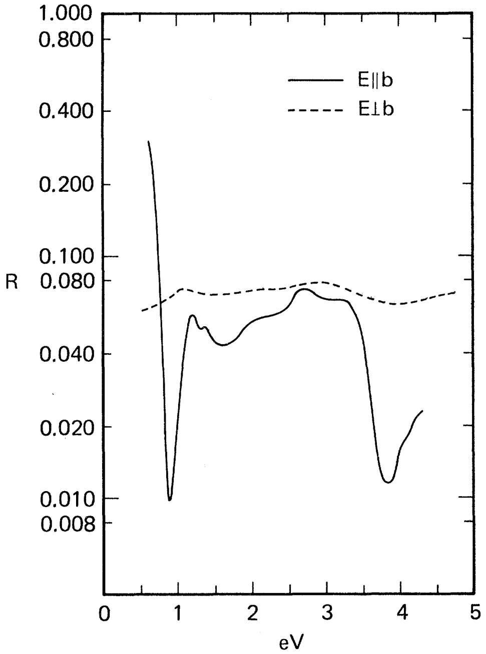

FIG. 1. Normal-incidence room-temperature reflectivity from the near infrared to the near uv for light polarized both parallel ($E \parallel b$) and perpendicular ($E \perp b$) to the conducting axis of TTF-TCNQ. Relative values of reflectance are accurate to within 0.001.

reflectivity spectrum for photon energies 0.6–4.5 eV of light polarized parallel and perpendicular to the conducting crystallographic *b* axis. The dominant feature is the Drude-like edge near 0.8 eV found only in the parallel direction.[9] This behavior is similar to that found in the mixed-valence Pt salts,[10] another class of quasi-one-dimensional metals. The higher-energy structure shown in Fig. 1 approximates that seen in other TCNQ salts[11] and most likely arises from intermolecular and/or intramolecular transitions. We will discuss the higher-energy data in a subsequent publication.

Figure 2 depicts the temperature dependence of the plasmalike edge from 20 to 300°K. Data were also taken at two temperatures in the vicinity of the purported Peierls distortion. These spectra merely interpolate between those already shown; no startling changes occurrred through the MI transition. Worth noting is the "blue shift" of the overall structure, the origin of which is presently unclear; however, it most probably arises from increases in bandwidth or electron density due to lattice contraction. A Drude fit to each temperature run was performed and the results are contained in Table I. The empirical equation employed was of the usual form, viz., $\epsilon_D(\omega)=\epsilon_0-\omega_p^2/\omega(\omega+i\tau^{-1})$, where τ is an energy-dissipating relaxation time, ω_p the plasma frequency, and ϵ_0 a real, frequency-independent, background dielectric constant. The ensuing best fit to our room-temperature data appears as a solid line in Fig. 2. The quality of the fit to the other temperature data is similar. The fits are uniformly poor in the vicinity of the minimum because of our neglect of the frequency dependence of ϵ_0 due to nearby molecular transitions. A most important caveat concerning spectral fitting procedures is in order. Seldom are the data adequate to permit selection of a unique model in the absence of independent physical knowledge concerning the underlying electronic structure. For example, we found we were able to fit our room-temperature data equally well, statistically, with a very strong Lorentzian oscillator of natural frequency 0.2 eV.

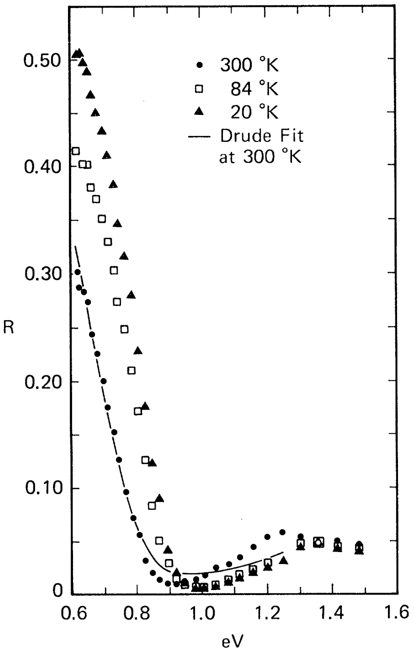

FIG. 2. Near-infrared reflectivity of incident light polarized parallel to the conducting axis of single-crystal TTF-TCNQ with temperature as a parameter.

Recenly, Torrance *et al.*[12] have observed a strong and broad absorption band centered at ~0.35 eV in TTF-TCNQ. This absorption is attributed to the excitation of correlated electron-hole pairs and is believed to give evidence that correlation effects may not be neglected in TTF-TCNQ. Thus, we cannot disregard the possibility that the Drude-like edge we observe has other than simple metallic origins.

The remarkable feature of our data is the relative insensitivity of τ, $\sigma_{\text{opt}}=\omega_p^2\tau/4\pi$, and the Drude edge to temperature. In vanadium dioxide, for example, occurrence of the MI transition leads to disappearance of the Drude edge.[13] One possible explanation for these results lies in a model first proposed by Philipp and Ehrenreich to deal with Drude-like effects in the uv reflectance of covalent semiconductors.[14] They show that for frequencies much greater than significant interband transitions, but less than *d*-shell or core excitations, valence electrons are essentially free, with dielectric response $\epsilon(\omega)=1-4\pi n_v e^2/$

TABLE I. Summary of Drude parameters and the optical conductivity obtained from fitting the data of Fig. 2. At room temperature $\sigma_{\text{dc}}\simeq 250\ \Omega^{-1}\ \text{cm}^{-1}$.

T (°K)	ϵ_0	ω_p (eV)	τ (10^{-15} sec)	σ_{op} (Ω^{-1} cm^{-1})
300	3.3	1.38	2.3	900
84	2.8	1.41	2.5	1020
67	2.9	1.44	2.7	1170
57	3.0	1.46	3.0	1300
20	3.2	1.52	3.0	1430

$m_e(\omega + i\tau^{-1})^2$, where n_v is the valence-band electron density and m_e is the free-electron mass. Provided the energy gaps opened up within the former conduction band are small, this argument also explains the remnant metallic reflectivity in TTF-TCNQ. Low-temperature conductivity data indicate that these gaps may be less than 0.1 eV.[1]

If the one-electron tight-binding approximation is valid for TTF-TCNQ, an estimate can be made of the conduction-band width from the measured plasma frequency.[15] This estimate depends greatly on the degree of overlap of the highest partially occupied TTF and TCNQ bands, or, put another way, on the amount of cation-anion charge transfer. Assuming a model of two overlapping tight-binding bands with equal τ's, we have two limiting cases. In one, both bands overlap such that the Fermi level bisects each respective band, and the relation $E_w = \hbar^2\omega_p^2/4n_c e^2 b^2$ is obtained, where n_c is the total two-band electron density, b is the lattice constant along the conductivity axis, and E_w represents a combined bandwidth. Taking our room-temperature value of ω_p, with lattice constant $b = 3.819$ Å and $n_c = 4.70\times10^{21}$ cm^{-1} as determined from the x-ray data, we obtain $E_w \sim 0.5$ eV. This result agrees with the value determined from thermoelectric-power data.[16] On the other hand, if the band overlap is small, we find that E_w in the above expression is the geometric mean of band overlap and band separation, and an estimate of the conduction bandwidth cannot be made.

For two overlapping half-filled bands, we note that $\hbar\omega_p > E_w$, and thus the states available for intra-conduction-band transitions will be exhausted before the plasma frequency is reached. This implies that the scattering times derived from the Drude fits are not necessarily characteristic of the scattering times involved in dc conductivity (these involve phonon-assisted transitions within kT of the Fermi level). The optical scattering may in fact be energy dependent near ω_p. It is not surprising then that different temperature dependences are observed for $\sigma_{\rm dc}$ and $\sigma_{\rm opt}$. Without more information we can only speculate on the origins of the differences in $\tau_{\rm dc}$ and $\tau_{\rm opt}$, since there are obviously many different ways a complex system like TTF-TCNQ can relax its electronic excitations other than through electron-phonon interactions. Coupling to molecular vibrations, impurity scattering, electron-electron scattering, and interchain scattering all could play a role.

There is further evidence that more than the electron-phonon interaction is responsible for both the optical and dc scattering times in our samples. Hopfield has shown[17] that two relations exist between the dimensionless electron-phonon coupling constant λ, the resistivity ρ, and the optical parameters ω_p and τ ($\tau^{-1} = \tau_{ep}^{-1} + \tau_{\rm other}$):

$$\lambda_1 = (\hbar/2\pi kT)\langle\tau_{ep}^{-1}\rangle, \quad \lambda_2 = (\hbar/2\pi k)\omega_p^2\,\partial\rho/\partial T.$$

Each equation applies only in the regime $T \gg \Theta$ (the Debye temperature of TTF-TCNQ is 89°K [7]). If only electron-phonon contributions to τ are important, then $\lambda_1 = \lambda_2$. From ω_p and τ given in Table I and $d\rho/dT = 1.3\times10^{-5}$ Ω cm/°K measured at room temperature, we find $\lambda_1 = 1.8$ and $\lambda_2 = 6.1$. We observe the temperature dependence of the dc resistivity to have both linear and quadratic terms, of which the latter is responsible for the anomalously large value of λ_2. It is clear then, that some unusual scattering mechanism is responsible for the dc resistivity.

How reliable is the estimate of λ_1? Taking λ_1 at face value would imply very strong electron-phonon coupling and would predict a high Peierls transition temperature ($T_{\rm P} > 500$°K).[5] However, the very small temperature dependence of $\tau_{\rm opt}$ shown in Table I suggests that λ_1 would be considerably smaller if only the electron-phonon contribution (τ_{ep}) to $\tau_{\rm opt}$ were used. We cannot estimate this contribution from our present data. However, it is certainly possible that τ_{ep}, and hence λ_1, are such as to give a $T_{\rm P}$ near the value predicted by Lee, Rice, and Anderson.[5] Similar difficulties in applying the Hopfield relations have been found in another anisotropic system, the superconducting transition-metal dichalcogenides, where the optical scattering time implies a much larger λ than does the superconducting transition temperature.[18] Bright, Garito, and Heeger[7] observe a temperature-dependent optical τ above 80°K which they attribute exclusively to electron-phonon scattering and from which they estimate $\lambda_1 = 1.3$. Based on our previous discussion it seems unlikely that $\tau_{\rm opt}$ is solely determined by electron-phonon interactions.

We wish to thank Dr. R. Schumaker and Dr. U. T. Mueller-Westerhoff for providing the source for the growth of TTF-TCNQ single crystals. The authors have benefited from conversations with Professor A. N. Bloch and Professor A. J. Heeger and thank the latter for communicating his optical results prior to publication.

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Relation between the Low-Temperature Thermal and Electrical Resistivities of Ag[†]

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(Received 28 August 1973)

Recent accurate measurements of the electrical resistivity of Ag above 2°K have permitted a reinterpretation of the published low-temperature thermal-conductivity data for silver. We report the discovery of an additional scattering process which may correspond to the phonon-assisted defect scattering proposed by Klemens.

Present theory, supported by various experimental results,[1] suggests that the low-temperature thermal resistivity of a monovalent metal may be represented reasonably well by an expression

$$W = \rho_0/L_0T + \rho_i/L_0T + \alpha T^2, \qquad (1)$$

where

$$\alpha T^2 = \frac{64.0}{497.6}\left(\frac{\theta_D}{T}\right)^2 \frac{\rho_n}{L_0 T}; \qquad (2)$$

W is the measured thermal resistivity, ρ_0 is the residual electrical resistivity, ρ_n is the electrical resistivity due to normal electron-phonon scattering, ρ_i is the ideal electrical resistivity (including umklapp processes), L_0 is the Sommerfeld value of the Lorentz number, and θ_D is the Debye temperature. The first term in (1) represents the impurity resistance, the second corresponds to the elastic scattering of electrons by phonons, and the third corresponds to the in-