# Single-Crystal Reflectance Studies of Tetrathiafulvalene Tetracyanoquinodimethane*

C. S. Jacobsen,† D. B. Tanner,‡ A. F. Garito, and A. J. Heeger
*Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174*
(Received 14 October 1974)

The polarized reflectance of single crystals of tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) at 300 K is reported over the frequency range 300 to 4000 $cm^{-1}$, with unpolarized data extending to 50 $cm^{-1}$. A Kramers-Kronig analysis is used to obtain the frequency-dependent conductivity $\sigma_1(\omega)$ and dielectric function, $\epsilon_1(\omega)$, for both $a$ and $b$ crystallographic axes. The results establish the existence of the energy gap and provide a quantitative measurement of the oscillator strength and relaxation time of the collective mode.

The existence of a gap[1] in the electronic excitation spectrum of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is of central importance to understanding the origin of the remarkable transport properties of this organic metal.[2-6] The energy gap in the infrared[1] ($E_g \simeq 0.14$ eV) together with the relatively large dc[2-4] and microwave[6] conductivities imply a correlated many-body state in which the low-frequency conductivity results from a collective mode. We report single-crystal reflectivity measurements in the range from 50 through 4000 $cm^{-1}$. The results confirm the energy gap as obtained from earlier work on thin films,[1] and place a lower limit on the collective-mode lifetime.

The infrared (ir) reflectivity measurements were preformed on single crystals ca. $2\times10$ $mm^2$ using as-grown surfaces.[7] ir spectra were recorded using a Perkin-Elmer 225 spectrophotometer over the region 300 to 4000 $cm^{-1}$, and a Grubb-Parsons Michelson interferometer in the range from 50 to 500 $cm^{-1}$. Figure 1 shows the polarized reflectance at room temperature for $E \| b$ and $E \| a$ in the range 300–4000 $cm^{-1}$. The dashed lines from 50 to 300 $cm^{-1}$ were obtained from unpolarized reflectance from carefully aligned single crystals; $\mathcal{R}(E \| b)$ was calculated by assuming that $\mathcal{R}(E \| a)$ is constant at the 300-$cm^{-1}$ value, so that $\mathcal{R}(E \| b) = 2\mathcal{R}_{\text{unpolarized}} - \mathcal{R}(E \| a)$. Throughout the ir, $\mathcal{R}(E \| a)$ is essentially frequency independent except for several sharp structures arising from intramolecular vibrations.

Over the intermediate ir, $\mathcal{R}(E \| b)$ has values of less than 72%, i.e., considerably below the values that would be expected from a simple metal with a dc conductivity[2-4] between 500–1000 $(\Omega\ cm)^{-1}$ and a plasma edge at 7000 $cm^{-1}$.[8-11] The relatively low reflectance at long wavelengths implies an energy gap $E_g = \hbar\omega_g$ with $\omega_g \tau_{sp} \sim 1$, where $\tau_{sp}$ is the single-particle scattering time appropriate to excitations near the gap edge.

Since the polarized reflectance is known for frequencies up to 37 000 $cm^{-1}$,[8-10] a Kramers-Kronig analysis is expected to give reliable results in the ir. This procedure consists of calculating the phase shift $\theta(\omega)$ from the dispersion relation:

$$\theta(\omega) = \frac{\omega}{\pi} P \int_0^\infty \frac{\ln \mathcal{R}(\omega') - \ln \mathcal{R}(\omega)}{\omega^2 - \omega'^2} d\omega'. \quad (1)$$

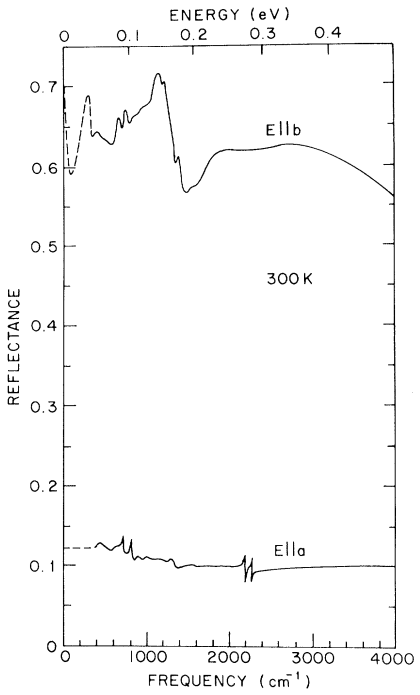


FIG. 1. Single-crystal reflectance of TTF-TCNQ. The curves labeled $E \| b$ and $E \| a$ represent polarized reflectance data with electric field vector parallel to the crystallographic $b$ and $a$ axes, respectively.

The complex index of refraction is then obtained from the inverted Fresnel formula

$$N = n + ik = [\epsilon_1 + i(4\pi/\omega)\sigma_1]^{1/2} = (1 + \mathcal{R}^{1/2}e^{i\theta})/(1 - \mathcal{R}^{1/2}e^{i\theta}). \quad (2)$$

Since $\mathcal{R}(\omega)$ is known for $50 < \omega < 37\,000$ cm$^{-1}$, conventional extrapolation procedures were employed.[12] In the range $0 < \omega < 50$ cm$^{-1}$, it was assumed that $\mathcal{R}(E \| b)$ behaves according to the Hagen-Rubens formula, $\mathcal{R} = 1 - A\omega^{1/2}$, with the parameter $A$ chosen so that a smooth connection with the data was obtained. The value for $\mathcal{R}(E \| a)$ was assumed constant in this range. The high-frequency extrapolation must simulate interband and (at very high frequencies) free-electron behavior. For the $b$-axis data we have used the standard approximation, $\mathcal{R}(\omega) = \mathcal{R}(\omega_c)(\omega_c/\omega)^P$, with $\omega_{c1} = 37\,000$ cm$^{-1}$, $P_1 = 2$ (corresponding to interband transitions), and with $\omega_{c2} = 2 \times 10^5$ cm$^{-1}$, $P_2 = 4$ (corresponding to free-electron behavior).

The frequency-dependent conductivity $\sigma_1(\omega)$ and dielectric function $\epsilon_1(\omega)$, as obtained from the Kramers-Kronig analysis, are shown for $E \| b$ and $E \| a$ in Figs. 2 and 3.

The insensitivity to the extrapolation procedures is illustrated by the following examples. Assuming $\mathcal{R}(E \| b)$ constant for $\omega < 50$ cm$^{-1}$ leads to changes in $\sigma_1$ less than 2% for $\omega > 500$ cm$^{-1}$, and gives in the gap region even lower values for $\sigma_1$ (the dotted curve below 200 cm$^{-1}$) than the Hagen-Rubens extrapolation (the dashed curve below 200 cm$^{-1}$). Assuming constant reflectance above 37 000 cm$^{-1}$ changes $\sigma_1{}^b(\omega)$ less than 10% for any $\omega < 10^4$ cm$^{-1}$, and has negligible effect below 500 cm$^{-1}$.

The main features in $\sigma_1{}^b(\omega)$ are a resonant structure with an absolute maximum at approximately 1100 cm$^{-1}$ with a relatively narrow minimum centered at approximately 1400 cm$^{-1}$. At higher frequencies a smooth, Drude-like frequency dependence is observed. The general shape and detailed structure are in excellent agreement with the thin-film data.[1] The larger peak value and narrower width of the single-crystal $\sigma_1{}^b(\omega)$ imply a longer single-particle scattering time, as expected.[8,9]

The corresponding behavior of $\epsilon_1{}^b(\omega)$ (Fig. 3) is that of an insulator with a transition across the energy gap sufficiently strong to give negative values between 1000 and 6000 cm$^{-1}$. At lower frequencies, $\epsilon_1{}^b$ is positive with a maximum of 82 near 300 cm$^{-1}$, while the detailed behavior in the far ir is not known. The general shape

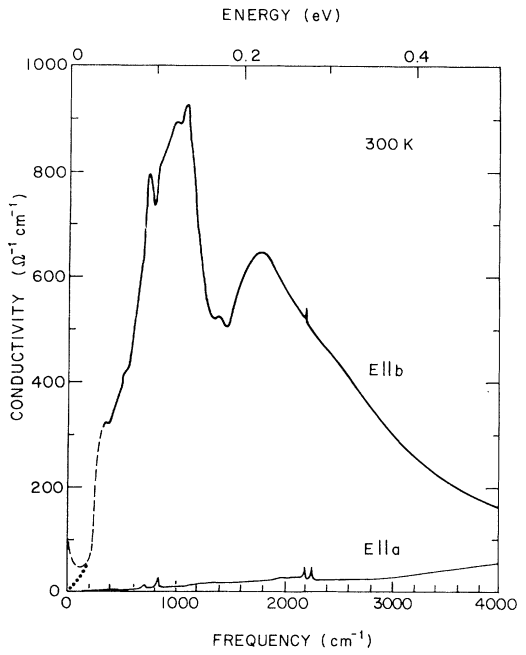


FIG. 2. The frequency-dependent conductivities $\sigma_1{}^b(\omega)$ and $\sigma_1{}^a(\omega)$ as obtained from Kramers-Kronig analysis. The dotted and dashed curves below 200 cm$^{-1}$ represent two different low-frequency extrapolations (see text).

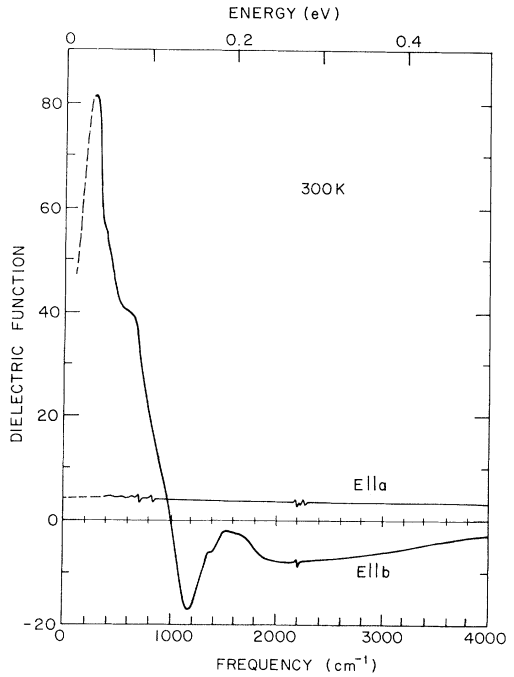


FIG. 3. The frequency-dependent dielectric functions $\epsilon_1{}^b(\omega)$ and $\epsilon_1{}^a(\omega)$ as obtained from Kramers-Kronig analysis.

and detailed structure are once again in excellent agreement with the thin-film data.[1]

The single-crystal reflectivity results thus establish the existence of the energy gap in the excitation spectrum. The gap is well defined even at room temperature where fluctuation effects would suggest a relatively high density of states in the gap region.[13] That there are states in the gap can be inferred from the magnetic susceptibility.[14-16] The susceptibility shows the qualitative features predicted by Lee, Rice, and Anderson,[13] and would imply that at room temperature the density of states near $E_F$ is within 20% of the unperturbed value. In contrast, $\sigma_1{}^b(\omega)$ in the gap region below 400 $cm^{-1}$ is more than an order of magnitude below the gapless Drude curve. We infer that the pseudogap in $\sigma_1(\omega)$ is in essence a mobility gap[17] caused by the strong dynamic fluctuations in local potential due to the inherent fluctuations in the one-dimensional system.

The *single-crystal* results for the frequency-dependent *b*-axis conductivity can thus be summarized as follows: (i) Zero frequency (dc): The conductivity is approximately $10^3$ $(\Omega\ cm)^{-1}$ at room temperature, increasing to values exceeding $10^4$–$10^5$ $(\Omega\ cm)^{-1}$ near 58 K.[2-4] (ii) Microwave frequency ($10^{10}$ GHz): The conductivity is approximately $10^3$ $(\Omega\ cm)^{-1}$ at room temperature, increasing to values exceeding $10^4$ $(\Omega\ cm)^{-1}$ near 58 K.[6] At both dc and microwave frequencies it appears likely that the peak conductivities are defect limited. (iii) Infrared frequencies: There is an energy gap[1] with magnitude $\hbar\omega_g \simeq 0.14$ eV above which the single-particle conductivity is Drude-like with a plasma frequency[8-11] of $\hbar\omega_p \simeq 1.2$ eV.

These results are sketched in Fig. 4, which is drawn to describe qualitatively the frequency dependence of $\sigma_1(\omega)$ near 60 K using typical values.

The collective-mode lifetime $\tau_c$ has not yet been measured directly. However, this width can be estimated from the collective-mode oscillator strength $\Omega_p{}^2$ and the measured dc conductivity, since[18] $\sigma_{\text{collective}} = (4\pi)^{-1}\Omega_p{}^2\tau_c$. An upper limit to $\Omega_p{}^2$ can be inferred from the single-crystal data. Since the width is less than the lowest measuring frequency, $\epsilon_1 = 100 - \Omega_p{}^2/\omega^2$. $\Re(E \parallel b)$ remains nearly constant at approximately 70% and does not begin to rise toward unity even in the range 50 to 100 $cm^{-1}$. Thus, we can conservatively construct the inequality $\Omega_p{}^2 < 10^6$ $cm^{-2}$ [a rapid rise toward $\Re(E \parallel b) \sim 1$ is required when $\epsilon_1 < 0$]. Using $\sigma_{dc}(300\ K) = 10^3$ $(\Omega\ cm)^{-1}$ leads to $\tau_c{}^{-1}(300\ K) < 3 \times 10^{12}$ $sec^{-1}$ (16 $cm^{-1}$). Assuming

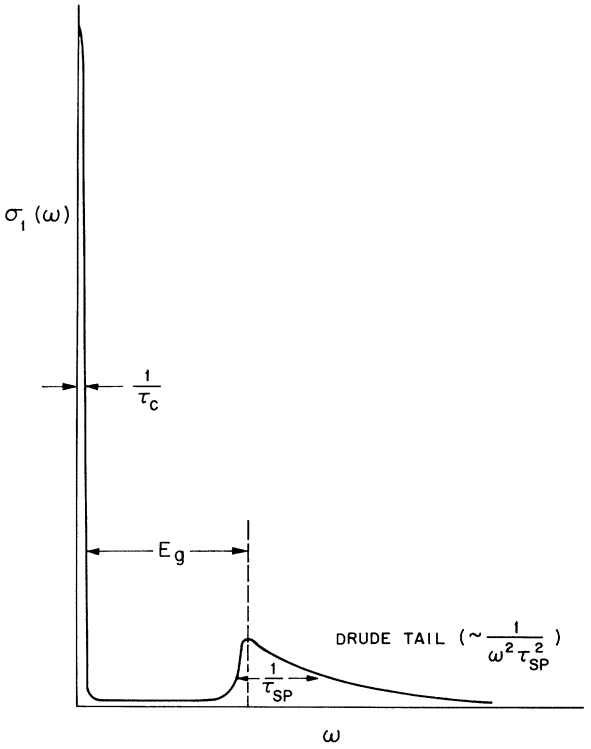


FIG. 4. Schematic diagram of $\sigma_1{}^b(\omega)$ for TTF-TCNQ as obtained from single-crystal data (see text). The curve is drawn using a typical value of $2 \times 10^4$ $(\Omega\ cm)^{-1}$ for the dc conductivity.

conservation of oscillator strength with decreasing temperature, a peak conductivity near 60 K in the range of $10^4$–$10^5$ $(\Omega\ cm)^{-1}$ implies $\tau_c{}^{-1}(60\ K) \sim 10^{11}$ $sec^{-1}$ (~0.5 $cm^{-1}$). Thus the collective-mode lifetime is enhanced over the single-particle scattering time by at least 2 orders of magnitude at room temperature and more than 3 orders of magnitude near 60 K. This comparison represents one of the clearest indications of coherence in the "metallic" state of TTF-TCNQ.

Much of the discussion surrounding the study of TTF-TCNQ and related systems centered on the dc electrical conductivity. However, it is now generally agreed that the intrinsic conductivity exceeds $10^4$ $(\Omega\ cm)^{-1}$ and there is evidence that the peak value exceeds $10^5$ $(\Omega\ cm)^{-1}$.[4] The sensitivity of the one-dimensional conductor to impurities and defects has been established,[4,6] so that these values may only be lower bounds. However, it is most important to view the dc and microwave conductivities in the context of the overall experimental knowledge of $\sigma_1(\omega)$ and $\epsilon_1(\omega)$ as obtained from single-crystal data and the earlier work on thin films.[1] TTF-TCNQ is not a

simple metal; it has the optical spectrum of a semiconductor, but conducts at zero frequency because of a long-lifetime collective mode.

*Work supported by the National Science Foundation through the Laboratory for Research on the Structure of Matter and Grant No. GH-39303, and by the Advanced Research Projects Agency through Grant No. DAHC 15-72C-0174.

†Present address: Physics Laboratorium III, The Technical University of Denmark, DK-2800 Lyngby, Denmark.

‡Present address: Physics Department, Ohio State University, Columbus, Ohio 43210.

[1]D. B. Tanner, C. S. Jacobsen, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 32, 1301 (1974).

[2]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).

[3]J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, J. Amer. Chem. Soc. 95, 948 (1973).

[4]M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1298 (1974).

[5]P. M. Chaikin, J. F. Kwak, T. E. Jones, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. 31, 601 (1973); J. F. Kwak, P. M. Chaikin, A. A. Russel, A. F. Garito, and A. J. Heeger, to be published.

[6]S. K. Khanna, E. Ehrenfreund, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 2205 (1974).

[7]These were all TTF-TCNQ($D_4$); the deuterated material grew into relatively large single crystals suitable for the infrared measurements.

[8]A. A. Bright, A. F. Garito, and A. J. Heeger, Solid State Commun. 13, 943 (1974).

[9]A. A. Bright, A. F. Garito, and A. J. Heeger, Phys. Rev. B 10, 1328 (1974).

[10]P. M. Grant, R. L. Greene, G. C. Wrighton, and G. Castro, Phys. Rev. Lett. 31, 1311 (1973).

[11]P. I. Perov and J. Fischer, Phys. Rev. Lett. 33, 521 (1974).

[12]See, for example, F. Wooten, *Optical Properties of Solids* (Academic, New York, 1972), p. 248.

[13]P. A. Lee, T. M. Rice, and P. W. Anderson, Phys. Rev. Lett. 31, 462 (1973).

[14]J. C. Scott, A. F. Garito, and A. J. Heeger, Phys. Rev. B (to be published).

[15]J. H. Perlstein, J. P. Ferraris, V. V. Walatka, D. O. Cowan, and G. A. Candela, in *Magnetism and Magnetic Materials—1972,* AIP Conference Proceedings No. 10, edited by C. D. Graham, Jr., and J. J. Rhyne (American Institute of Physics, New York, 1973), p. 1494.

[16]Y. Tomkiewicz, B. A. Scott, L. J. Tao, and R. S. Title, Phys. Rev. Lett. 32, 1363 (1974).

[17]A similar analysis leading to the inference of a mobility gap in $K_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ (KCP) has been presented by H. R. Zeller (private communication).

[18]M. J. Rice, S. Strässler, and W. R. Schneider, in "Saarbrücken Conference on One-Dimensional Conductors," Saarbrücken, Germany, June 1974, edited by H. G. Schuster (Springer, Berlin, to be published).

# From Giant Moment to Kondo and Spin Glass Behavior: The Electrical Resistivity of *Pd*Fe and (*Pd*Fe)H

J. A. Mydosh

*Institut für Festkörperforschung der Kernforschungsanlage, D-517 Jülich, Germany*

(Received 1 October 1974)

I have measured the low-temperature electrical resistivity $\rho(T)$ for a series of *Pd*Fe alloys with and without hydrogenation. For Pd + 0.2 at.% Fe, the sharp decrease in $\rho(T)$ at the Curie temperature gives way to a broad Kondo-like minimum. With increasing Fe concentration, the giant-moment ferromagnetism is severely hindered by hydrogen charging, and $\rho(T)$ shows the characteristics of an interacting Kondo system or a "spin glass."

Palladium-iron is a well-known giant-moment system which orders ferromagnetically with small amounts of iron ($c \gtrsim 0.1$ at.% Fe).[1-3] On the other hand, elemental Pd can be easily charged with large amounts of hydrogen and becomes superconducting for H/Pd $\gtrsim 0.75$.[4,5] It has further been established that the large exchange-enhanced Pauli paramagnetic susceptibility of Pd linearly decreases with hydrogenation, and at H/Pd $\approx 0.65$ a slightly negative or diamagnetic susceptibility is found.[6] Recent theories[7,8] have considered this result as a necessary (but not sufficient) condition for the rather high superconducting transition temperature ($\approx 9$ K) of palladium hydride.[5]

As the exchange enhancement of Pd and the giant moments of *Pd*Fe lead to large effects in the electrical resistivity,[9,10] any modification of the Pd matrix polarizability should be strongly reflected in $\rho(T)$ and $d\rho(T)/dT$. Furthermore, the hydrogenation of *Pd*Fe is especially signifi-