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
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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. 2×10 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 τ_{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:

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

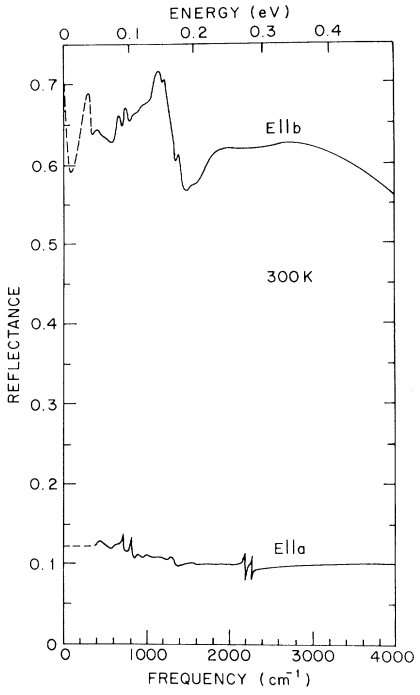

FIG. 1. Single-crystal reflectance of TTF-TCNQ. The curves labeled $E \| b$ and $E \| a$ represent polarized reflectance data with electric field vector parallel to the crystallographic b and a axes, respectively.

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 σ_1 less than 2% for $\omega > 500$ cm^{-1}, and gives in the gap region even lower values for σ_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

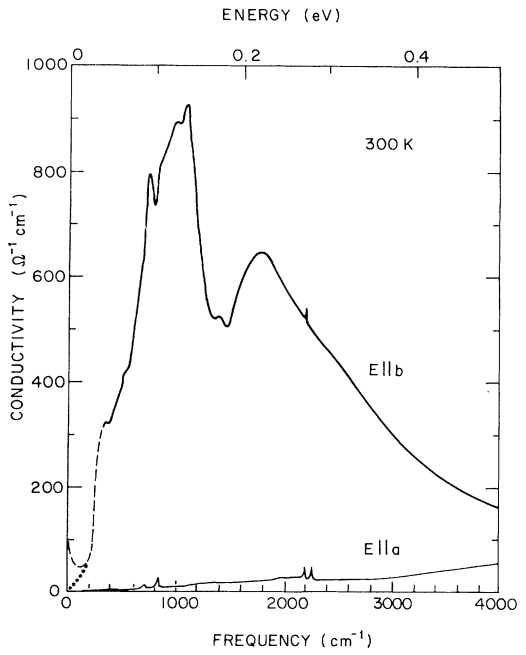

FIG. 2. The frequency-dependent conductivities $\sigma_1{}^b(\omega)$ and $\sigma_1{}^a(\omega)$ as obtained from Kramers-Kronig analysis. The dotted and dashed curves below 200 cm^{-1} represent two different low-frequency extrapolations (see text).

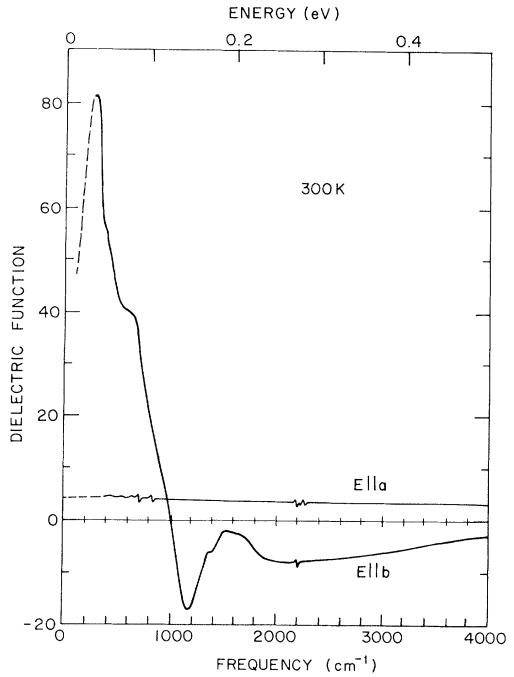

FIG. 3. The frequency-dependent dielectric functions $\epsilon_1{}^b(\omega)$ and $\epsilon_1{}^a(\omega)$ as obtained from Kramers-Kronig analysis.

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 τ_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

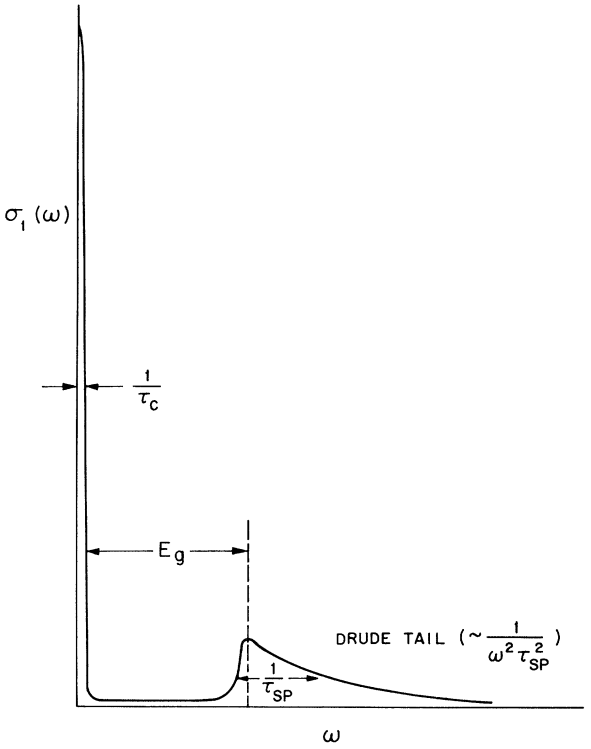

FIG. 4. Schematic diagram of $\sigma_1{}^b(\omega)$ for TTF-TCNQ as obtained from single-crystal data (see text). The curve is drawn using a typical value of 2×10^4 $(\Omega\ cm)^{-1}$ for the dc conductivity.

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.

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

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

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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
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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 ≈ 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 (≈ 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-