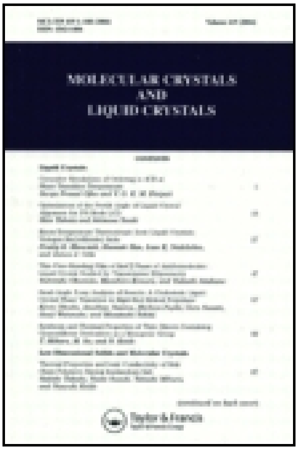

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Low Temperature Infrared Studies of TTF-TCNQ

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Version of record first published: 14 Oct 2011.

To cite this article: D. B. Tanner & C. S. Jacobsen (1982): Low Temperature Infrared Studies of TTF-TCNQ, Molecular Crystals and Liquid Crystals, 85:1, 137-145

To link to this article: http://dx.doi.org/10.1080/00268948208073639

Mol. Cryst. Liq. Cryst., 1982, Vol. 85, pp. 137–145
0026-8941/82/8501-0137$06.50/0

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

LOW TEMPERATURE INFRARED STUDIES OF TTF-TCNQ

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Submitted for publication December 18, 1981

Polarized infrared reflectance measurements have been made on TTF-TCNQ single crystals at temperatures between 25 K and 300 K. Measurements were made for frequencies between 7 cm^{-1} (1 meV) and 20,000 cm^{-1} (2.5 eV). These measurements support a charge density wave mechanism for the high dc conductivity of TTF-TCNQ and provide estimates for the 60 K lifetime and the low-temperature pinning frequency of the charge density wave. A value, 300 cm^{-1} (0.04 eV), for the semiconducting energy gap is also obtained.

I. INTRODUCTION

In this paper we describe the chain-axis optical properties of TTF-TCNQ at temperatures between 25 K and 300 K. These data were obtained from polarized reflectance measurements that spanned the frequency range between 7 cm^{-1} (1 meV) and 20,000 cm^{-1} (2.5 eV). The results are in reasonable agreement with previous polarized reflectance studies of this material.[1–4] They indicate that at low temperatures the low energy electronic properties of TTF-TCNQ are dominated by charge density wave (CDW) effects.[5–10] At 25 K, in the insulating regime, a pinned CDW phase mode is seen at 40 cm^{-1} and there is a very sharp peak at 250-300 cm^{-1} resulting from excitations across the single-particle gap.[11] At 60 K the dc conductivity is dominated by the sliding CDW or Fröhlich mode; the energy gap is smeared by thermal effects. At 300 K single-particle effects are at least as important as collective effects and no well-defined gap is observed. In addition, at all temperatures there is evidence for coupling of conduction electrons to molecular vibrations.[12]

CDW phenomena arise from the Peierls instability in linear-chain materials. This instability produces a periodic variation of conduction electron charge density along the one-dimensional chain and induces an energy gap at the Fermi surface. When the wavelength of the CDW is incommensurate with the lattice constant (as is the case for TTF-TCNQ[13,14]), it is possible to have a sort of superconductivity first described by Fröhlich: under the influence of an applied field, the CDW can move rigidly through the lattice and contribute to the dc conductivity. The lifetime of this current-carrying collective mode should be comparable with the lifetime of a low energy phonon and should be much longer than the lifetime of a single-particle electronic excitation.

This Peierls-Fröhlich viewpoint leads to very definite predictions for the optical properties of a one dimensional metal.[15] At high temperatures, the frequency dependent conductivity should be single-particle-like; the conductivity should be that of a Drude metal with effective mass equal to the band mass and carrier scattering time equal to the single particle lifetime. Once the Peierls instability has set in (perhaps 150 K in TTF-TCNQ[14]), there should be a gap in the single-particle spectrum; the dc conductivity is due to a long-lived sliding CDW which has a relatively high effective mass. At the lowest temperatures, the CDW is pinned by three-dimensional interactions, which always occur in any real material; the gap in the single-particle spectrum persists but instead of high dc conductivity there is a pinned CDW mode at very low frequencies. This pinned mode is an oscillation in the CDW phase (i.e. in the location of the CDW relative to the underlying lattice).

II. EXPERIMENTAL DETAILS

The polarized reflectance of TTF-TCNQ single crystals was measured using a Michelson interferometer in the far-infrared region and a grating monochromater at higher frequencies.[16] The samples were cooled in an Air Products Helitran continuous flow refrigerator. The far-infrared measurements were made with a mosaic which consisted of nine TTF-TCNQ single crystals, each ∿1.2 by 0.15 cm in size. The higher frequency measurements were made on one of these large crystals. Reference spectra were obtained by measuring the reflectance of gold-coated mosaics (in the far infrared) or crystals (at higher frequencies). By comparing the signal reflected by a sample to that reflected from the same sample coated with gold, accurate values for the reflectance could be obtained.

The sample temperature was inferred from the dc resistance[17] of one of the crystals in the mosaic. This calibration was important because radiation from the spectrometer and from the room heated the sample, causing it to remain at a higher temperature than indicated by the thermometer in the Helitran. The offset at low temperatures was large: the thermometer indicated 6 K; the sample temperature was 25 K.

III. RESULTS

Figure 1 shows the b-axis reflectance of TTF-TCNQ at 25 K, 60 K and 300 K. The plasma edge is clearly seen between 5000 cm^{-1} and 7000 cm^{-1} at all three temperatures. There is considerable structure in the reflectance between 300 cm^{-1} and 2200 cm^{-1}, the region where the TTF and TCNQ molecules have their frequencies of internal vibration.[18] At 300 K and 60 K the far-infrared reflectance has negative slope and approaches unity as the frequency goes to zero, as expected for a good conductor. In contrast, the 25 K reflectance has a very strong feature between 40 cm^{-1} and 300 cm^{-1}; below 40 cm^{-1} the reflectance has positive slope.

The temperature dependence of the reflectance at higher frequencies consists of a sharpening of the plasma edge and an increase of the reflectance with decreasing temperature. At 500-600 cm^{-1} the 25 K reflectance is nearly unity.

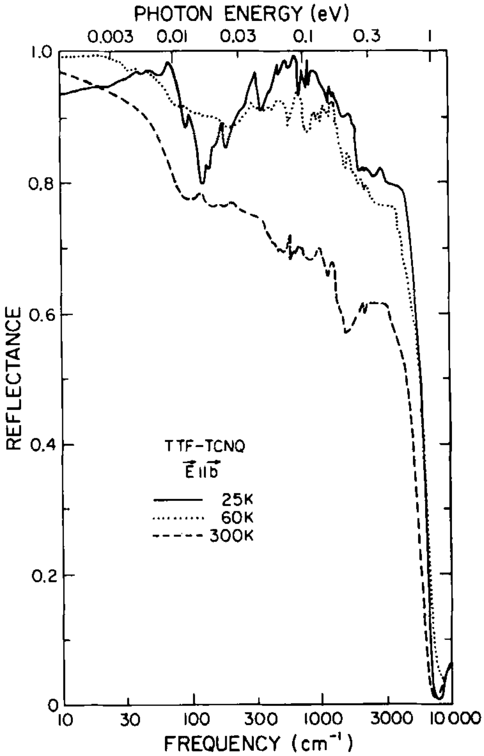


FIGURE 1. Reflectance of TTF-TCNQ for electric field along the b-axis. Data are shown on a logarithmic frequency scale from 10 cm^{-1} to 20,000 cm^{-1} for three temperatures: 25 K, 60 K and 300 K.

IV. DISCUSSION

We have used Kramers-Kronig analysis[19] of the reflectance to obtain frequency dependent conductivity, $\sigma_1(\omega)$, (Figure 2) and the real part of the dielectric function, $\varepsilon_1(\omega)$, (Figure 3). These curves have many features, which we will describe one at a time in the following subsections.

A. Room Temperature Conductivity

On a scale that extends from zero to 10^4 Ω^{-1} cm^{-1}, the 300 K conductivity does not vary much. The low frequency value is 900 Ω^{-1} cm^{-1}, in agreement with the dc conductivity.[17] There is a broad dip in the infrared and a small peak around 800-1000 cm^{-1}.

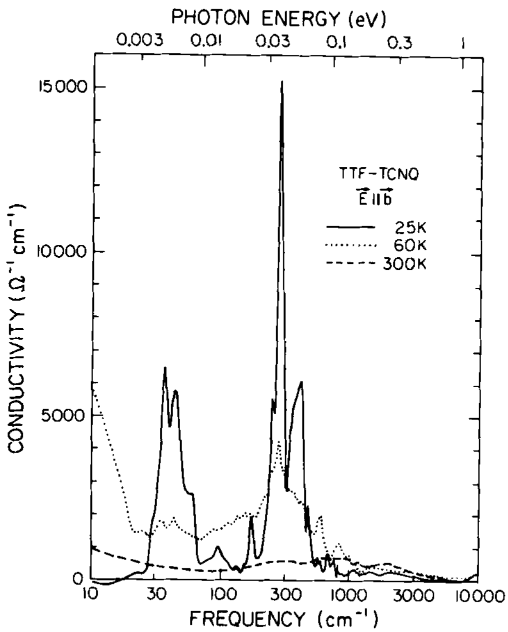


FIGURE 2. The frequency dependent conductivity of TTF-TCNQ between 10 cm^{-1} and 20,000 cm^{-1}. Note the logarithmic frequency scale. Data are shown for temperatures of 25 K, 60 K and 300 K.

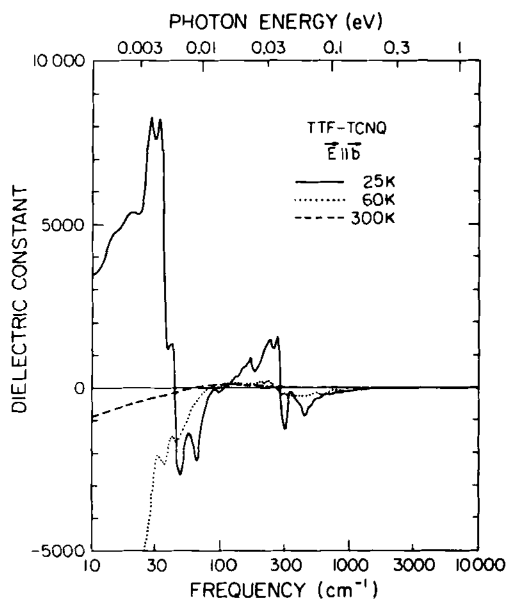


FIGURE 3. The real part of the dielectric function of TTF-TCNQ between 10 cm^{-1} and 20,000 cm^{-1}. Note the logarithmic frequency scale. Data are shown for temperatures of 25 K, 60 K and 300 K.

B. Electron-molecular Vibration Interaction

Many antiresonances or dips occur in the 300 K conductivity. Each of these dips occurs near the frequency of an Ag vibration of either the TTF or TCNQ molecule;[18] these data suggest that electron-molecular vibration interactions[12] play an important role in the electronic properties of TTF-TCNQ. Most of these features are seen in the 60 K and 34 K spectra as well.

C. Charge-density Wave Phenomena

The conductivity at 60 K has a strong maximum at the lowest frequencies. This maximum extrapolates to give a 60 K dc conductivity of between 6000 Ω^{-1} cm^{-1} and 10,000 Ω^{-1} cm^{-1}, in good agreement with the dc conductivity of good but not extraordinary TTF-TCNQ crystals.[17] We attribute this narrow zero frequency peak in the conductivity to a sliding CDW. The conductivity quickly falls to around 1000 Ω^{-1} cm^{-1}; this value probably represents the single-particle contribution to the 60 K conductivity.

The 25 K conductivity is $\sim$0 Ω^{-1} cm^{-1} at 10 cm^{-1}. A strong peak appears at 40 cm^{-1}, which we attribute to the charge density wave, now pinned by the three-dimensional ordering which occurs in TTF-TCNQ at 38 K. (Only below 38 K do we see evidence for the pinned mode in our far-infrared data.) The pinning frequency is higher than previously suggested[20,21] for TTF-TCNQ; the pinned mode is, however, relatively unambiguous in our data.

The effective mass of the CDW can be inferred from the oscillator strength sum rule. As described in an earlier publication,[4] this sum rule gives at 25 K an effective mass of $\sim$80 m_e or $\sim$20 m^* (m_e is the free electron mass and m^* is the band mass). The lifetime of the sliding CDW at 60 K can then be calculated to be 1.6×10^{-12} sec by assuming a Drude form for the CDW conductivity. Alternately, the lifetime can be inferred for the width of the peak in $\sigma_1(\omega)$ at zero frequency. The full width at half maximum is $\sim$10 cm^{-1}; the width corresponds to a lifetime of $\sim 5 \times 10^{-13}$ sec. In contrast, at the plasma edge[22] $\tau_{sp} \sim 6 \times 10^{-15}$ sec. There are two orders of magnitude difference between the lifetime of the CDW and of single particle excitations at the plasma frequency.

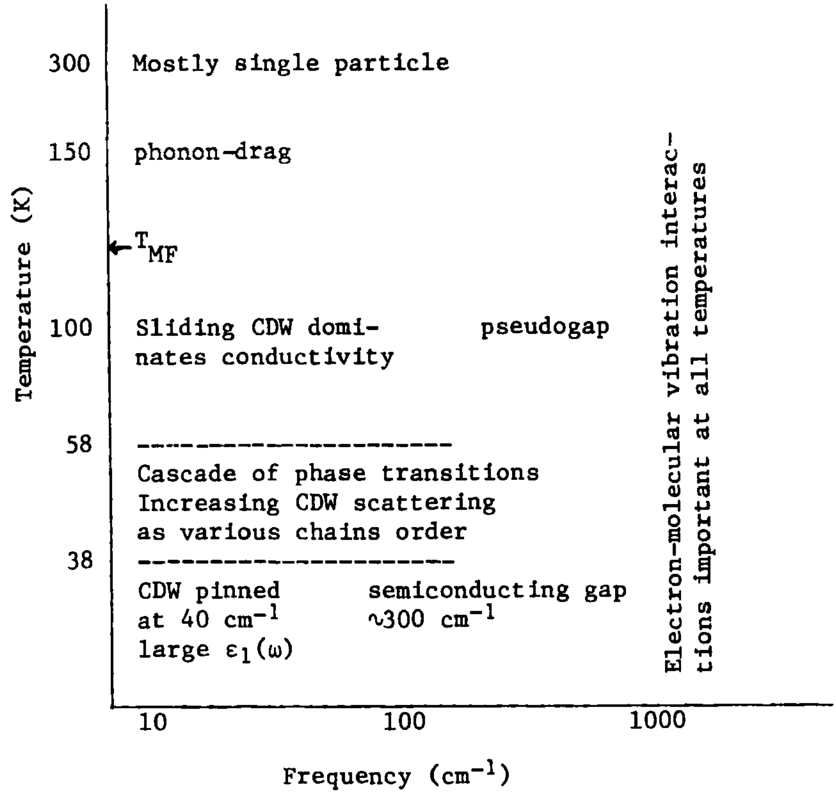
The 25 K real dielectric function has as its dominant feature the structure between 20 cm^{-1} and 100 cm^{-1} associated with the CDW. The zero frequency value of $\varepsilon_1(\omega)$ is 3200, in good agreement with microwave measurements.[23] At 60 K and above the low frequency dielectric constant is negative, consistent with the finite dc conductivity at these temperatures.

D. The Energy Gap

The 25 K $\sigma_1(\omega)$ has a very strong narrow maximum at $\sim$300 cm^{-1}. The width of this peak is only 200 cm^{-1}. This feature is probably the single-particle energy gap in TTF-TCNQ. With $2\Delta \sim 300$ cm^{-1}, the mean-field Peierls transition temperature $T_p \simeq 2\Delta/3.5 \simeq 130$ K. This value is consistent with many other estimates. The gap structure is still present (though somewhat smeared) at 60 K but is almost completely washed out at 300 K. Note, however, that at all temperatures $\varepsilon_1(\omega)$ is positive for a substantial range of far-infrared frequencies. At 300 K, this range extends from $\sim$60 cm^{-1} to $\sim$500 cm^{-1}. A positive dielectric constant is the signature of an absence of free-carrier excitations in this frequency or energy range.

V. CONCLUSIONS

Our data support the picture of TTF-TCNQ as a Peierls-Fröhlich conductor. The high dc conductivity around 60 K and the high microwave dielectric constant around 25 K result from charge-density wave effects. A sort of phase diagram of the electronic structure of TTF-TCNQ on temperature frequency axes can be inferred from our data, along with conductivity,[17] resonance,[24] and structural[14] studies. It is shown on the top of the next page.



ACKNOWLEDGEMENTS

The beautiful crystals which we have used were grown by I. Johannsen and L. Groth-Andersen. This work was supported by the Danish Natural Sciences Research Council and the NATO Research Grants Program.

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