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Optical Properties and Band Structure of (TSeF)(TCNQ) Compared to (TTF)(TCNQ). B. WELBER, P. M. GRANT, P. E. Seiden, and E. M. Engler, IBM Research Laboratories--We have analyzed the plasma energies of (TSeF)(TCNQ) and (TTF)(TCNQ) as obtained from optical reflectivity and Drude fitting in order to estimate the absolute bandwidths of the cation and anion chains in these two isostructural materials. Upon decomposing the measured plasma energies, aided by the $TCNQ^-$ chain transfer integral calculated by Berlinsky, et al.,[1] we find the TTF bandwidth in (TTF)(TCNQ) to be slightly larger than that of the anion suggesting that the d-function contribution to the cation overlap cannot be neglected. For (TSeF)(TCNQ), we find the cation bandwidth to be 2-3 times that of the (TCNQ) chain. We use these results to calculate the dc conductivity and Pauli susceptibility to be expected in each material on the basis of tight-binding band theory and an electron-electron scattering model and compare the results with experimental values.

[1]A. J. Berlinsky, J. F. Carolan and L. Weiler, Solid State Commun. 15, 795 (1974).

Submitted by

Signature of APS Member

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Coulomb interactions between the excess electrons on the same and neighboring sites of TCNQ chains in charge transfer salts. These estimates are used to motivate a model of the electronic structure of these salts. Some preliminary theoretical results and interpretations of experimental data on the basis of this model are described.
*Submitted by Jerry B. Torrance.

BJ 5 Resistive Fluctuations in Nearly One-Dimensional Conductors.* P. M. HORN and D. GUIDOTTI, Univ. of Chicago, and T. CARRUTHERS and A. N. BLOCH, Johns Hopkins U.--We examine the electrical resistivities of a variety of nearly one-dimensional organic conductors including TTF-TCNQ, TSF-TCNQ, TMTTF-TCNQ and TMTSF-TCNQ. In the region of phase transitions, the temperature dependence of the electrical resistivity varies strikingly from material to material. We compare these experiments with the results of a simple model calculation for the temperature dependence of the electrical resistivity in a system of weakly coupled one-dimensional electron-phonon chains. In the approximations considered, the scattering contribution to the resistivity is treated in the Born approximation while Peierls fluctuations are included using simple power counting and universality arguments. Comparison between experiment and theory suggests that many of the qualitative and quantitative differences between various materials results from the influence of inter-chain coupling on the fluctuation dimensionality.

*Work supported by NSF-MRL.

BJ 6 High Resolution Conductivity Measurements on TTF-TCNQ and Related Compounds.* T. Carruthers, A. N. Bloch, and D. O. Cowan, Johns Hopkins U.--We report the results of new low frequency ac conductivity measurements on TTF-TCNQ and related compounds as a continuous function of temperature T. Preliminary measurements indicate that the high-temperature resistivity of TTF-TCNQ consists of two distinct regions: for 75 K < T < ~150 K the temperature-dependent component of the resistivity varies as $T^{2.0}$; for T > ~150 K it varies as $T^{2.5}$. Hysteresis associated with the 38 K first-order phase transition persists from approximately 34 K to 47 K. These results are correlated with excess noise measurements and with published diffuse X-ray and neutron scattering data. Similar measurements on compounds related to TTF-TCNQ are reported.

*Supported in part by Materials Science Office, Advanced Research Projects Agency, Department of Defense.

BJ 7 Anistropy in dc Conductivity and Its Pressure Dependence in an Isostructural Family of Organic Conductors.* J. R. Cooper and D. Jerome Universite Paris-Sud, Orsay France, +S. Etemad Arya-Mehr University, Tehran Iran, E. M. Engler IBM Research Center, N.Y. The three components of the room temperature dc conductivity σ_b, σ_a, and σ_c, of TTF-TCNQ and its Selenium analogs, TSeF-TCNQ and DSeDTF-TCNQ, for pressures upto 10K bar have been measured. The anisotropy factors σ_b/σ_a and σ_b/σ_c are basically the same for the three compounds and have a room temperature value of order of 10^3 and 10^2, respectively. Under isotropic pressure the three components of the conductivity increase rapidly with the same rate of $\partial \ln \sigma/\partial p = .27$ per Kbar in TTF-TCNQ. The same behavior is also observed in TSeF-TCNQ but with a different rate of $\partial \ln \sigma/\partial p = .16$ per Kbar We note that the observed pressure independent anisotropy cannot be readily understood in terms of the widely accepted picture for the conduction process in TTF-TCNQ and TSeF-TCNQ; ie, the conduction process along the chains is metallic and perpendicular to the chains is diffusive.

* Submitted by Farhad Ardalan.
+ Work carried out in parts at Universite Paris-Sud, Orsay.

BJ 8 Current Flow Irregularities in TTF-TCNQ Measured with the Scanning Electron Microscope. JAMES P. LONG, JOHN ARAO, G. DEPASQUALI, and CHARLES P. SLICHTER, U. of Illinois,† Urbana-Champaign.--We report a new technique for studying electrical conductivity. A moveable current source provided by the electron beam of a scanning electron microscope is used to map the potential distribution on surfaces containing the a-b axes of single crystals of TTF-TCNQ. Silver paint contacts are used to return the beam current to ground, and to measure voltage changes as the beam position is moved. On several samples, data were measured both by this technique and by the conventional moveable contact method. Our data reveal irregularities in current flow which arise from sample cracks and from inhomogeneities in the silver paint contacts. We discuss the condition under which such two-dimensional potential plots can be used to determine the conductivities in the a and b directions. We also discuss the effects which the observed irregularities can produce in conventional four-probe and Montgomery-type[1] conductivity measurements.
†Supported by ERDA-EY-76-C-02-1198.
[1]H.C. Montgomery, J. Applied Physics 42, 2971 (1971).

BJ 9 Raman Spectra of TTF Crystals. H. TEMKIN and D. B. FITCHEN, Cornell University* and F. WUDL, Bell Laboratories. -- TTF (tetrathiofulvalene), the donor molecule of the charge transfer salt TTF-TCNQ, crystallizes from solution in the form of bright orange needles. The stacking of TTF molecules in TTF and TTF-TCNQ is very similar. In the molecular crystal there are two TTF molecules per primitive cell, space group $P2_1/c$, site group D_{2h}. We have measured the Raman spectrum of crystals (~1mm dia) of TTF using a rhodamine 6G dye laser, at temperatures down to 2K. At 2K nine external modes (widths 1.5 - 2.5 cm^{-1}) are observed between 27 and 119 cm^{-1}. Nineteen internal modes are observed between 251 and 1730 cm^{-1}, with the strongest line at 1516 cm^{-1}. C-H stretch lines are found between 3040 and 3100 cm^{-1}. These features are only partially resolved at room temperature. In addition to the Raman features an emission spectrum is seen. At 2K this consists of three overlapping broad bands at 1.99, 1.96, and 1.82 eV. Each of these bands has associated with it a sharp zero-phonon line and a similar set of sharp one-phonon lines.
*Work supported by NSF through Materials Science Center at Cornell.

BJ 10 Theory of the DC Conductivity of Weakly Pinned Fröhlich-Charge-Density-Wave Condensates at Low Temperatures.* S.E. TRULLINGER, Univ. Southern Calif., A.R. BISHOP, Queen Mary College, London, R.A. GUYER, Univ. of Mass., Amherst and J.A. KRUMHANSL, Cornell Univ.-- We discuss a phenomonological theory of the low-temperature DC conductivity of weakly-pinned Fröhlich charge-density-wave condensates using a Fokker-Planck equation as the starting point. We find that at low fields the conductivity is dominated by ϕ-particles and that as the electric field is increased the conductivity becomes strongly nonlinear. Comparison of preliminary calculations with recent data[1] on TTF-TCNQ will be made.

*Research supported in part by ERDA, Contract No. E(11-1)-3161 and by NSF.
[1]Marshall J. Cohen, et al., Phys. Rev. Lett. 37, 1500 (1976).

BJ 11 Optical Properties and Band Structure of (TSeF)(TCNQ) Compared to (TTF)(TCNQ). B. WELBER, P. M. GRANT, P. E. SEIDEN, and E. M. ENGLER, IBM Research Laboratories-- We have analyzed the plasma energies of (TSeF)(TCNQ) and (TTF)(TCNQ) as obtained from optical reflectivity and Drude fitting in order to estimate the absolute bandwidths of the cation and anion chains in these two isostructural materials. Upon decomposing the measured plasma energies, aided by the TCNQ chain transfer integral calculated by Berlinsky, et al.,[1] we find the TTF bandwidth in (TTF)(TCNQ) to be slightly larger than that of the anion suggesting that the d-function contribution to the cation overlap cannot be neglected. For (TSeF)(TCNQ), we find the cation bandwidth to be 2-3 times that of the (TCNQ) chain. We use these results to calculate the dc conductivity and Pauli susceptibility to be expected in each material on the basis of tight-

binding band theory and an electron-electron scattering model and compare the results with experimental values.

[1] A. J. Berlinsky, J. F. Carolan and L. Weiler, Solid State Commun. 15, 795 (1974).

BJ 12 Electronic Structure of TTF-TCNQ and TSeF-TCNQ. F. HERMAN, IBM San Jose Research Laboratory. -- Starting with scattered wave calculations of the dimers and trimers of TTF[1], TCNQ[2], and TSeF, the intrachain transfer integrals and bandwidths of the anion and cation stacks in TTF-TCNQ and TSeF-TCNQ were calculated. The dependence of the various bandwidths on the stacking distances were also determined. Some of the optical properties of these crystals, including their pressure dependence, will be interpreted in terms of simple energy band pictures.

[1] D. R. Salahub, R. P. Messmer, and F. Herman, Phys. Rev. B 13, 4252 (1976).

[2] F. Herman, D. R. Salahub, and R. P. Messmer, to be published.

BJ 13 The Energy-Band Gaps in TTF-TCNQ, measured by Far-Infrared Photoconductivity* J.E. ELDRIDGE, University of British Columbia - The b-axis photoconductivity of TTF-TCNQ at 5 K has been measured with polarized radiation in a Michelson interferometer. The highly-structured bolometric response from active vibrational modes was suppressed by increasing the chopping frequency and reducing the temperature. The onset of strong photoconductivity clearly gives an intrinsic band-gap of about 300 cm^{-1} (±20 cm^{-1}) (430 K, 37 meV) for both E||a and E||b. For E||b, additional weak photoconductivity is observed between 90 cm^{-1} and 300 cm^{-1}, with a spectrum characteristic of impurities. The 90 cm^{-1} (129 K, 11 meV) impurity energy-gap corresponds to the d.c. conductivity activation-energy of our samples at 5 K, while the intrinsic 300 cm^{-1} gap agrees with our d.c. conductivity results above about 12 K. This implies an approximate impurity concentration of a few parts per million. It is hoped to shortly determine the bandwidth of the E||a photoconductivity, which should be much less than for E||b.

BJ 14 Anisotropic Conductivity of $Na_xV_2O_5$-β.* R.H. WALLIS, and N. SOL, Thomson-C.S.F., Orsay, France.-- The β-phase Vanadium bronzes $Na_xV_2O_5$ exhibit anisotropic transport properties due to electrons donated by the Sodium to the Vanadium chains. Typically, at 300K, along the chains $\sigma_{//} \simeq 100\Omega^{-1}cm^{-1}$ whereas $\sigma_{\perp} \simeq 1\Omega^{-1}cm^{-1}$; also, at low temperatures, a $T^{-1/3}$ variable range hopping conductivity is observed perpendicular to the chains.[1] Single crystals with variable electron density ($0.20 \leq x \leq 0.33$) have been grown, and their transport properties will be reported.

* Submitted by A. ZYLBERSZTEJN

[1] A. Friederich, D. Kaplan, N. Sol, R.H. Wallis and A. Zylbersztejn, XIIIth Int. Conf. on the Physics of Semiconductors, Rome (Aug.30-Sept.3, 1976).

SESSION BK: SUPERCONDUCTIVITY: THIN FILMS, TUNNELING, PROXIMITY EFFECT

Monday afternoon, 21 March 1977
Santa Fe Room at 2:00 P.M.
M.R. Beasley, presiding

BK 1 Supercooling Magnetic Field of Paramagnetically Limited Al Films. P.M. TEDROW and R. MESERVEY, Francis Bitter National Magnet Laboratory*, M.I.T. -- The superconducting-to-normal transition of very thin Al films below a certain temperature T_1 and in high magnetic fields is of first order because of the effects[1] of spin paramagnetism. Thus the second order critical field which can be calculated from the Ginzburg-Landau equations is the supercooling field in this temperature range. Measurements have been made of the fluctuation conductivity of these films allowing determination of the supercooling field as a function of temperature. Comparison of the measurements with the theory will be made.

*Supported by the National Science Foundation.

1. A review of the properties of paramagnetically limited superconductors can be found in P. Fulde, Adv. in Phys, 22, 667(1973).

BK 2 Properties of Cryogenically Condensed Films of Ga in High Magnetic Fields. R. MESERVEY, P.M. TEDROW, and D. PARASKEVOPOULOS, Francis Bitter National Magnet Laboratory*, MIT -- The parallel and perpendicular critical magnetic fields of cryogenically condensed Ga films were measured as a function of temperature. Tunneling conductance vs. voltage measurements were also made with an Al counterelectrode at magnetic fields up to 15 Teslas. The results are compared to theory. In some instances the films, which were formed at about 1 K, were annealed to above 10 K at which temperature the resistance greatly decreased, but when the films were recooled to 1 K the paramagnetic limiting remained unchanged.

*Supported by the National Science Foundation.

BK 3 Far Infrared Properties of Thin Film High Temperature Superconductors.* S. W. MCKNIGHT, R. H. THORLAND†, and S. PERKOWITZ, Emory U.--We have measured the reflection and transmission of thin films[1] (300 to 4000 Å) of Nb, V_3Si, and Nb_3Ge between 20 and 200 cm^{-1}. The results at 300 K could be explained by a Drude model complex conductivity $\sigma_1 + i\sigma_2$ in the extreme dirty limit, with $\sigma_1 = \sigma_{DC}$ and $\sigma_2 = 0$. Transmission measurements near the superconducting transition in V_3Si gave structure similar to that seen previously in bulk material.[2]

*Work supported by NSF grant DMR75-13917.
†Present address: Volunteer State Community College, Gallatin, Tennessee.
[1] Samples provided by L. R. Testardi, Bell Labs.
[2] S. Perkowitz, M. Merlin, and L. R. Testardi, Solid State Commun. 18, 1059 (1976).

BK 4 The Effect of Substrate and Annealing on High T_c Superconducting Nb-Ge Films. G. W. WEBB*† and J.J. ENGELHARDT, †UCSD. --Results are presented on high T_c Nb-Ge films of thickness ~ 10 μ deposited onto a variety of planar substrates by chemical vapor deposition. Among the substrates onto which some specimen adhesion has been found are alumina, sapphire of two orientations, niobium and molybdenum. Comparison of the T_c of these specimens with free standing deposits (flaked from lithium niobate) suggests that T_c is depressed by differential thermal contraction between deposit and substrate; deposits on Mo, the substrate with greatest thermal mismatch, show the largest T_c depression of over 1 K. Some deposits on high strength 7 μ diameter graphite fibers display unusual breaks which apparently arise from differential thermal contraction. Low temperature annealing of deposits has not been found to increase T_c under the conditions investigated. For example, free standing deposits and deposits on alumina, both with T_c onsets above 22 K were found to have their T_c unchanged or depressed by ~0.1 K after being annealed at 725°C for 3 months.

*Supported by NSF Grant DMR75-04019.
†Supported by NASA Grant NSG-3055.

BK 5 Superconductivity in Ultrathin Pb Films Deposited on Silicon.* D. L. MILLER, Brookhaven National Lab.-- Superconducting Pb films 11Å to 200Å thick were deposited in ultrahigh vacuum on the clean (111) surface of crystalline silicon. Measurements of normal state film resistivity and of the superconducting transition temperature T_c were taken in situ. The dependence of T_c on film thickness was essentially identical to that previously measured for Pb films grown epitaxially on crystalline PbTe. A microcrystalline model is developed

OBJECTIVES

- ESTIMATE CATION CHAIN BANDWIDTHS
  (d-FUNCTION CONTRIBUTION TO OVERLAP)

- COMPUTE ENHANCEMENT FACTORS FOR MEASURED SPIN SUSCEPTIBILITIES

- INDEPENDENTLY EVALUATE BOTH CHAIN BANDWIDTHS SELF-CONSISTENTLY FROM MEASURED VALUES OF THERMOPOWER, PLASMA ENERGY, AND CHARGE TRANSFER

PROGRAM

ASSUME KNOWN TCNQ BANDWIDTHS :

$$(4t)_{TCNQ} \approx 0.5 \text{ eV} \quad \text{(HERMAN, et al., BERLINSKY, et al.}$$

↓

COMPUTE TCNQ CHAIN PLASMA ENERGY

$$(\hbar\omega_p)_A^2 = \frac{4e^2 (4t)_A b^2}{V} \sin \rho\pi/2$$

↓

COMPUTE CATION CHAIN PLASMA ENERGY

$$(\hbar\omega_p)_c^2 = (\hbar\omega_p)_{exp}^2 - (\hbar\omega_p)_A^2$$

↓

COMPUTE CATION BANDWIDTH

↓

DO CHAIN PAULI SUSCEPTIBILITIES

$$\chi_p = \mu_B^2 L / \pi t \sin \rho\pi/2$$

↓

CHAIN ENHANCEMENTS

$$f = \chi_s^{exp} / \chi_p$$

TWO BAND DRUDE MODEL

$$\epsilon(\omega) = 1 - \frac{(\omega_p^2)_c}{\omega(\omega + i/\tau_c)} - \frac{(\omega_p^2)_A}{\omega(\omega + i/\tau_A)}$$

SINGE DRUDE APPROXIMATION

TARGET EXPRESSION:

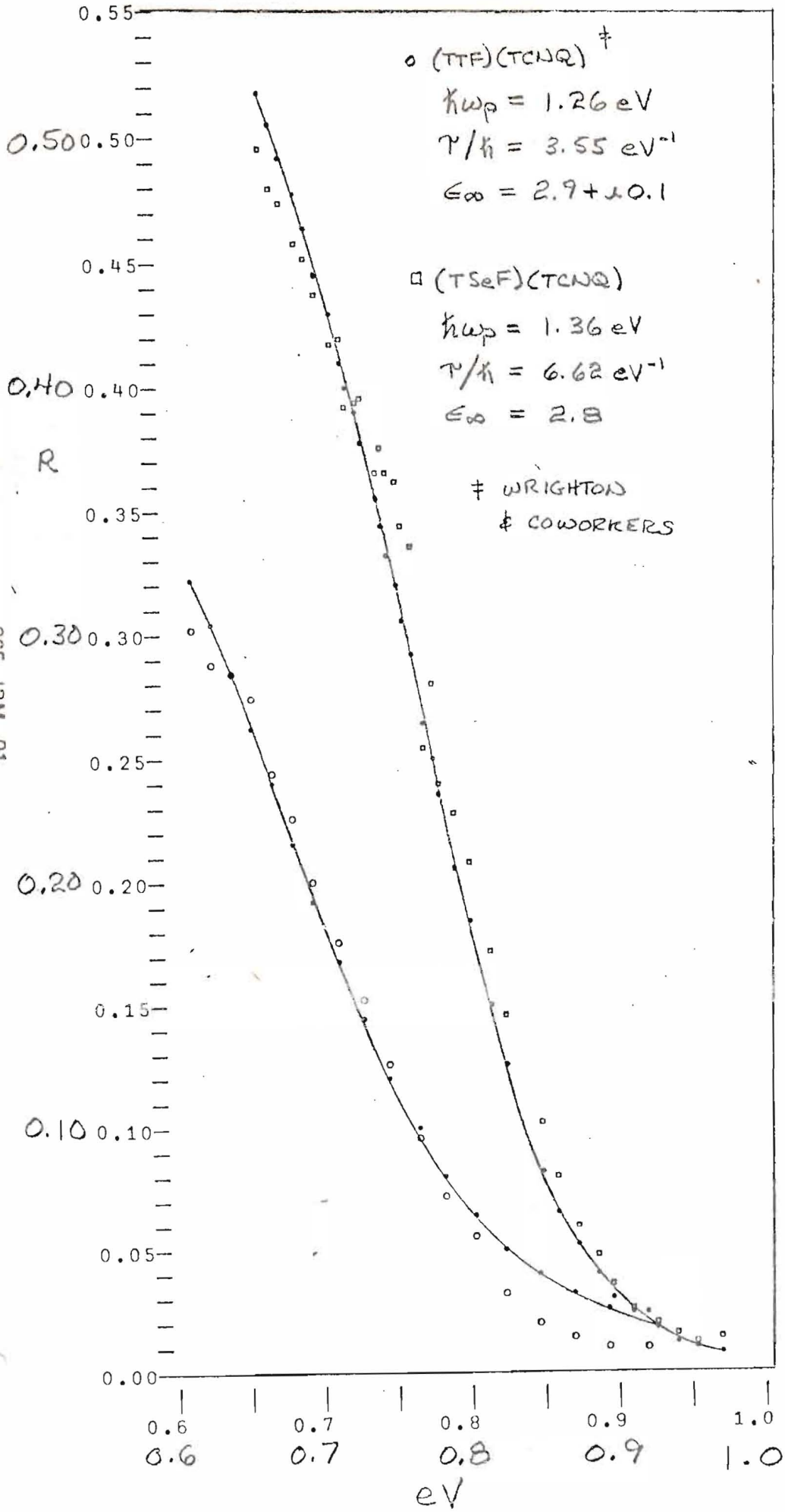
$$\epsilon(\omega) = 1 - \frac{(\omega_p^2)_{eff}}{\omega(\omega + i/\tau_{eff})}$$

VALID WHEN: $\omega, \omega_p > 1/\tau_A, 1/\tau_c$

THEN:

$$(\omega_p^2)_{eff} = (\omega_p^2)_c + (\omega_p^2)_A$$

$$\frac{1}{\tau_{eff}} = \frac{(\omega_p^2)_A/\tau_A + (\omega_p^2)_c/\tau_c}{(\omega_p^2)_A + (\omega_p^2)_c}$$


o (TTF)(TCNQ) ‡
ħω_p = 1.26 eV
τ/ħ = 3.55 eV⁻¹
ε∞ = 2.9 ± 0.1
□ (TSeF)(TCNQ)
ħω_p = 1.36 eV
τ/ħ = 6.62 eV⁻¹
ε∞ = 2.8
‡ WRIGHTON & COWORKERS
R
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.6
0.7
0.8
0.9
1.0
eV

	TTF-TCNQ	TSeF-TCNQ
ω_p (eV)	1.26	1.36
S (μV/°K)	−27	+3
ρ	0.59	0.63
B_D (eV)	0.41	0.59
B_A (eV)	0.61	0.56
σ ($1/\Omega$-cm)	1800	3400

$$\sigma \sim B^4 \rho^3$$

$$S \sim B^{-1}$$

$$S_T = \frac{S_D \sigma_D + S_A \sigma_A}{\sigma_D + \sigma_A}$$