Pressure dependence of the Drude optical edge of tetrathiafulvalenium (TTF) and tetraselenafulvalenium (TSeF) tetracyanoquinodimethanide (TCNQ)

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We have measured the pressure dependence of the Drude absorption edge in tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ) and tetraselenafulvalenium-tetracyanoquinodimethanide (TSeF-TCNQ) over the range of 0–60 kbar. The plasma frequency and optical conductivity are extracted from the data using a model which explicitly considers the two-stack nature of these materials. The pressure dependence of the plasma frequency is found to agree fairly well with that expected from a simple tight-binding model. The optical conductivity can be decomposed by a Mathiessen's rule technique in the manner typically used for the temperature dependence of the dc conductivity. To experimental accuracy, the temperature-independent term in the optical conductivity is also pressure independent. A calculation of the conductivity in terms of the electron-electron interaction yields a pressure dependence equal to that observed.

I. INTRODUCTION

It is now well established that the optical properties of the conducting charge transfer salts of TCNQ are, like their transport properties, strongly anisotropic and display a metallic Drude-like reflectance edge only for polarizations along the molecular stacking axis of the crystals.[1] These edges have usually been analyzed by fitting them to the well-known expressions arising from a Drude free-electron model for the bulk dielectric constant.[2] The parameters thus obtained are the plasma frequency ω_p containing information on the total conduction-electron bandwidth, the scattering time τ related to the various relaxation processes of the Drude excitations, and a background dielectric constant representing all dispersive effects outside the range of free-electron excitation energies. The plasma frequency and scattering time can be combined to give the optical conductivity expressed by the simple relation

$$\sigma = \omega_p^2 \tau / 4\pi. \tag{1}$$

The temperature dependence of ω_p and τ has been determined and the implications for the temperature dependence of the dc conductivity have been actively discussed.[1,3] However, no similar investigation of the pressure dependence of the Drude parameters and subsequent comparison to existing dc data has yet been undertaken. We now report such measurements for TTF-TCNQ and TSeF-TCNQ and discuss them in the light of existing calculations of the bandwidths for these two materials. We find that the pressure dependence of the intrinsic part of the optical conductivity is as large as that obtained at dc. We then interpret the pressure dependence of the dc and optical conductivities by using an electron-electron scattering model for the free-electron relaxation process and show that this model can account for the unusually high-pressure dependence observed.

II. EXPERIMENTAL RESULTS

The samples used were single-crystal platelets measuring $0.2\times0.3\times0.02$ mm^3 in the a, b, c^* directions, respectively. The pressure apparatus employed was of the diamond anvil type with the hydrostatic medium consisting of equal parts of n-pentane and isopentane contained within the cylindrically shaped volume bounded by the anvil surfaces and the inside of a hard steel gasket. The high-pressure cell and associated optical equipment were adaptations of a system previously applied to absorption measurements on very small samples.[4] The principal modification was that the lower diamond on which the sample rests is now coated with a highly reflecting silver film to serve as the incident light standard. The upper diamond functions as both an entrance and an exit window. Furthermore, the distance between anvils was increased sufficiently to assure that reflections from the diamond-liquid interface would not reach the detector. Since the space inside the pressure cell is limited, the sample size is necessarily quite small. This fact limits the total signal available and care must be taken with the whole optical system to maximize the resultant signal.

The light source used was a 75-W xenon high-pressure concentrated arc lamp. Not only is this source brighter than larger lamps of its type, but

it is also nearly an order of magnitude brighter than filament-type sources in the near-infrared region. Moreover, its exceptional stability and long lifetime greatly simplify the collection of data. The light was focused onto a pinhole and then concentrated onto the sample in a cone whose effective numerical aperture was about 0.15 corresponding to angles of incidence from 0° to 9°.

A wide spectral range is needed for these experiments since we wish to cover the whole Drude edge, even when shifted with pressure. Therefore, we require photon energies from at least 0.6 to 3.5 eV. To cover this range we employed two separate spectrometers, one for the range 0.6–1.5 eV equipped with a cooled PbS detector, and the second for the visible range equipped with a cooled RCA 31034 photomultiplier–phonon-counter combination.

The incident light was polarized using a Glan-Thomson prism, and the resulting extinction ratios exceeded several thousand even at elevated pressures, showing that despite the considerable strain produced in the diamond window, there were no significant effects on the measurements due to induced birefringence.

Light intensities I_s and I_0, from the sample and silver reference surface, respectively, were recorded on a recorder. However, in the regions where the lamp spectrum is sharply peaked, data were taken point by point at the specific wavelengths of the peaks and valleys only. It should be remarked that the stability of the entire system was such that no significant mismatch was encountered when comparing two sets of data on the same sample providing due care was exercised to use the identical portions of the cell in both runs.

In analyzing the reflectance data, account must be taken of the pressure dependence of the refractive index of the pressure fluid. The refractive index of the pentane mixture used in our experiments is strongly pressure dependent, rising from a value of 1.32 at ambient to 1.68 at 62 kbar. Absolute pressures throughout the experiment were determined from the fluorescence shift of the R emission lines from ruby chips comounted with the sample. Further details of the apparatus and optical system can be found elsewhere.[5]

The reflectivity data for TTF-TCNQ and TSeF-TCNQ are presented in Figs. 1 and 2, respectively. The shift of the edge with pressure is clear and a careful inspection of the figures will show that the edge also becomes sharper with pressure.

In order to relate theory and experiment, which we will do in Sec. IV, we must also know the compressibility of these compounds. Debray *et al.*[6] have measured the lattice parameters of TTF-TCNQ as a function of pressure up to 20 kbar by neutron diffraction. They have noted that the behavior of the lattice parameter is very similar to that of sodium. In Fig. 3, we show the data of Debray *et al.*[6] along with a Bridgman-type[7] fit to the data. The three points above 30 kbar have been measured by us by directly measuring the change in sample size under a microscope. It can be seen that these data are consistent with the Bridgman fit to the neutron data. We have no high-pressure data in the c direction since it was along the line of sight of the optical beam. The solid curves of Fig. 3 will be used for the analysis of Sec. IV. We will also use these curves for TSeF-TCNQ, because of the similarity of the materials and the lack of direct measurements.

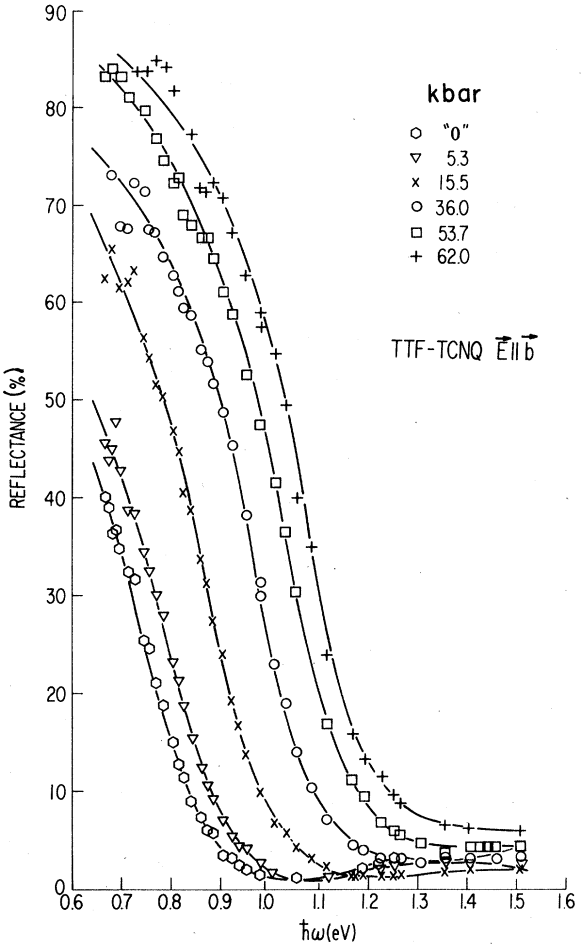

FIG. 1. Pressure dependence of the plasma reflectance edge of TTF-TCNQ.

III. OPTICAL DATA ANALYSIS

The complex dielectric function for a metal can be written as follows

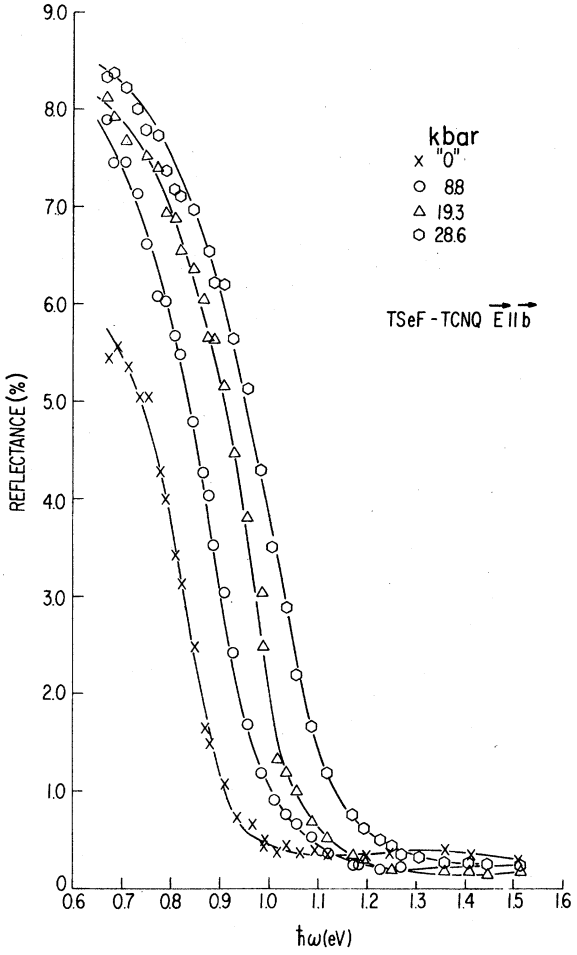

FIG. 2. Pressure dependence of the plasma reflectance edge of TseF-TCNQ.

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} + \sum_{\{j\}} \frac{\omega_{pj}^2}{\omega_j^2 - \omega^2 + i\omega/\tau_j}, \tag{2}$$

where $\{j\}$ represents the set of quantum numbers pertinent to the nonmetallic states of the material. The labeled parameters ω_{pj}, ω_j, and τ_j in the third term represent the oscillator strength, transition frequency, and lifetime of each optical transition between these states, respectively. The simple Drude model is obtained by lumping the sum term in Eq. (2) into a single background dielectric quantity ϵ_∞ assumed constant within the frequency range of metallic optical activity. This gives the well-known three-parameter Drude expression

$$\epsilon(\omega) = \epsilon_\infty - \omega_p^2/\omega(\omega + i/\tau). \tag{3}$$

For the case of TTF-TCNQ and TSeF-TCNQ, where both donor and acceptor stacks conduct, Eq. (3) must be expanded and rewritten as

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_{p_D}^2}{\omega(\omega + i/\tau_D)} - \frac{\omega_{p_A}^2}{\omega(\omega + i/\tau_A)}, \tag{4}$$

where D and A denote donor and acceptor, respectively. The experimental values of the reflectance can then be related to Eq. (4) through the usual formulas involving the complex index of refraction and the Fresnel equations for normal incidence reflectivity. In practice it turns out to be difficult, within experimental error, to distinguish between a reflectance curve originating from Eq. (3) and one arising from Eq. (4). It would be particularly convenient from an analytical point of view if one could fit the experimental data to Eq. (3) and at the same time have an algebraic expression relating its parameters to those of Eq. (4). The following equations,

$$\omega_p^2 = \omega_{p_D}^2 + \omega_{p_A}^2, \tag{5}$$

$$\omega_p^2/\tau = \omega_{p_D}^2/\tau_D + \omega_{p_A}^2/\tau_A \tag{6}$$

can be shown to connect Eqs. (3) and (4) to third order in ω^{-1} providing $\omega_p, \omega > \tau_D^{-1}, \tau_A^{-1}$. These conditions are in fact met in TTF-TCNQ and TSeF-TCNQ. Therefore, Eq. (5) permits us to quantitatively relate band parameters calculated for separate segragated stacks to a single experimental plasma frequency.

IV. DISCUSSION

A. Plasma frequency

The plasma frequency as a function of lattice parameter is shown in Fig. 4. In a tight-binding model the plasma frequency for a single band can be expressed as

$$\omega_p^2 = \frac{4e^2}{\hbar^2} \frac{b}{ac} B \sin\tfrac{1}{2}\pi\rho_C, \tag{7}$$

where a, b, and c are the lattice parameters, B is the bandwidth, and ρ_C is the charge transfer. Using Eq. (5), we then have

$$\omega_p^2 = (4e^2/\hbar^2)(b/ac)(B_D + B_A)\sin\tfrac{1}{2}\pi\rho_C \tag{8}$$

for the two-band model appropriate to the systems considered here.

We can now use this equation to deduce one of the stack bandwidths given an estimate of the other and the experimentally determined plasma frequency. This is a useful exercise in view of the uncertainty concerning the relative role of chalcogenide d functions of the cation bandwidths in these materials.[8] If we accept 0.6 eV as the generally agreed upon calculated value[8,9] for the TCNQ bandwidth in both TTF-TCNQ and TSeF-

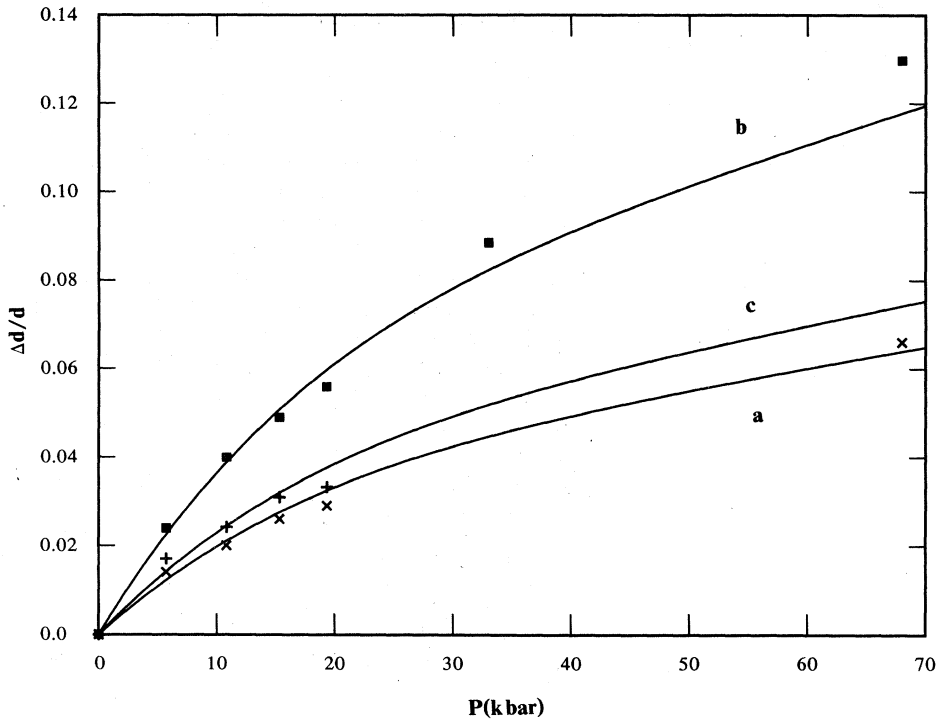

FIG. 3. Pressure dependence of the lattice constants of TTF-TCNQ in the a (×), b(■), and c(+) directions.

TCNQ, and use as their experimental plasma energies 1.2 and 1.4 eV, respectively, Eq. (8) yields, with inclusion of appropriate charge transfers and lattice parameters, 0.5 eV for TTF and 0.6 eV for TSeF. These are in good agreement with the results of Herman and co-workers whose self-consistent cluster calculations included chalcogenide d functions. We conclude that overlap of these functions play an important role in the determination of cation bandwidths in the TTF family of

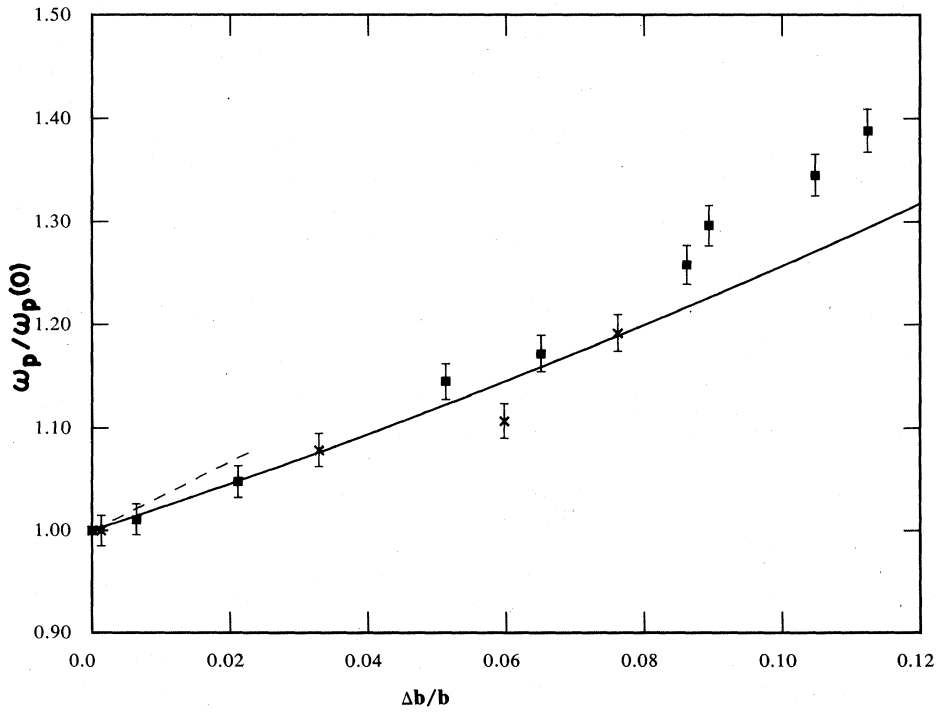

FIG. 4. Plasma frequency (ω_p) as a function lattice parameter in the b direction for TTF-TCNQ(■) and TSeF-TCNQ(×). The solid line is for constant charge transfer and the dashed line includes the change in charge transfer found from diffuse x-ray measurements.

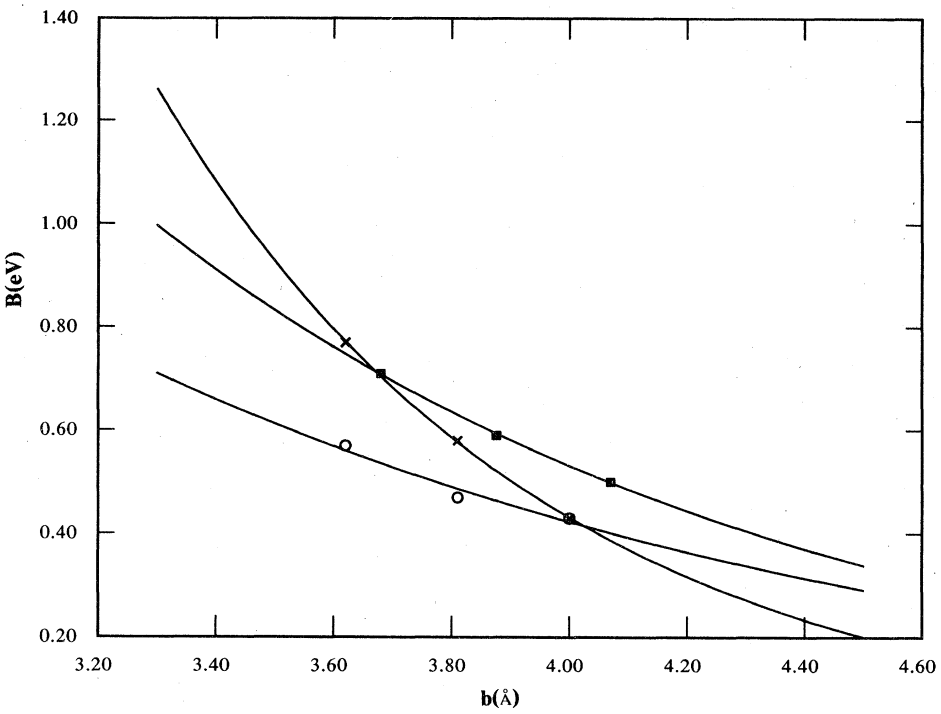

FIG. 5. Bandwidth as a function of lattice parameter in the b direction for TTF (○), TSeF (■), and TCNQ (×) [after Herman (Ref. 9)].

conducting charge transfer salts.

Given these promising results at $P=0$, we are encouraged to go even further and use the calculated pressure dependencies of both stack bandwidths[8,9] to try and fit, through Eq. (8), the measured pressure dependence of ω_p. Figure 5 shows the stack bandwidth pressure dependencies found by Herman *et al.*[9] The calculated points are for the observed intermolecular spacing and ±5% of that spacing. The curves shown are quadratic fits to the three calculated points, and are used for extrapolation to values outside the calculated range.

The solid line in Fig. 4 is a plot of Eq. (8) incorporating the bandwidths given by Fig. 5. The fit is quite good up to about $\Delta b/b = 0.09$ (40 kbar) after which the observed plasma frequency increases faster than would be expected. This result could have at least two simple explanations. Firstly, the bandwidths could increase faster with decreasing lattice parameter than shown in Fig. 5. The discrepancy is outside the region calculated by Herman so that our extrapolation may not be valid. The bandwidth need only be about 20% larger than that given in Fig. 5 in order to account for the difference. This is certainly within the range of possibility. Secondly, we have assumed that the charge transfer is independent of pressure. An increase of the charge transfer would also result in an increase in the plasma frequency. This is very unlikely to be the case here, however, since it would require the charge transfer in TTF-TCNQ to increase from 0.59 to 1.0, an extremely large change.[10]

B. Conductivity

The optical conductivity (and/or resistivity) is given by Eq. (1). In analogy with the dc resistivity, it has been shown[3] that one can likewise decompose the temperature dependence of the optical resistivity by Mathiessen's rule.[11] In fact, one can write this decomposition in the following general way:

$$\rho(\omega, T, P) = \rho_0(\omega, P) + A(P)T^2, \tag{9}$$

where both the exponent and coefficient of the T^2 term were shown to be the same for the dc and optical cases.[3] However, we are now faced with the problem of determining the pressure dependence of $\rho_0(\omega, P)$.

Since we do not know the temperature dependence of the optical conductivity for nonzero pressures, we take the following approach. We will assume Eq. (9) to be valid at each pressure and use the experimentally measured pressure dependence of the dc conductivity[12-14] to determine ρ_T (i.e., AT^2). We then perform the decomposition and see what we obtain for ρ_0. The results, in terms of the normalized conductivity, are shown for TTF-TCNQ

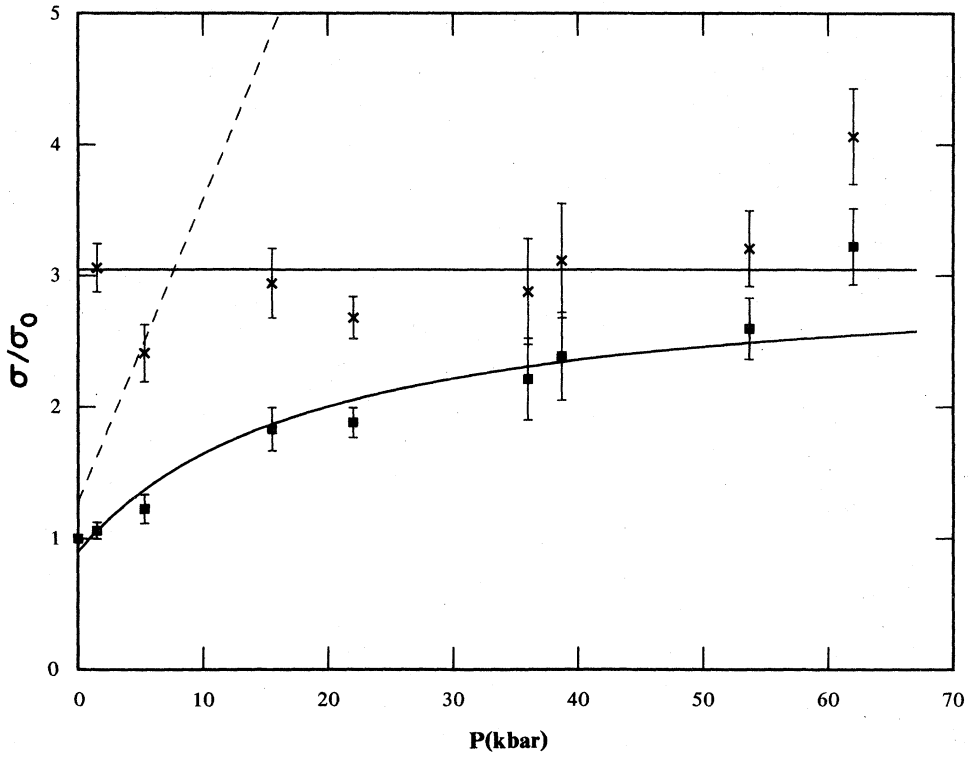

FIG. 6. Decomposition of the optical conductivity of TTF-TCNQ; σ_{opt} (■), σ_{dc} (---), σ_0 (×) are shown. The solid lines are fits to the points with σ_0=const.

in Fig. 6 and for TSeF-TCNQ in Fig. 7. Although the errors are considerably larger here than for the plasma frequency, it can clearly be seen that a constant ρ_0 is a good fit to the results. Therefore, the optical data is consistent with Eq. (9), the dc data, and $\rho_0(\omega, P) = \rho_0(\omega)$.

The magnitude of ρ_0 is much larger at optical frequencies than dc. This is reasonable since

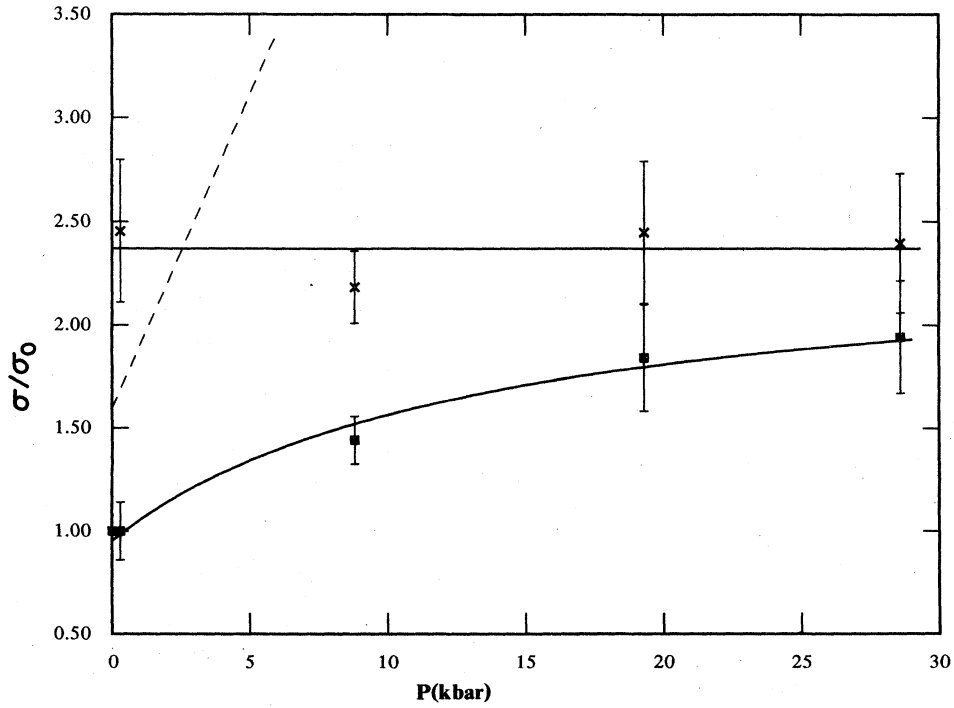

FIG. 7. Decomposition of the optical conductivity of TSeF-TCNQ; σ_{opt} (■), σ_{dc} (---), σ_0 (×) are shown. The solid lines are fits to the points with σ_0=const.

many more decay channels can exist for Drude excitations than the simple scattering mechanisms operative at dc. That is, Eq. (9) at optical frequencies really represents a decomposition of the Drude τ^{-1} into a dc part $[A(P)T^2]$ and a part $[\rho_0(\omega)]$ representing relaxation through relatively pressure- and temperature-independent optical phonon, molecular vibration, or interband transition states, or a combination of these. The subject of electron-molecular vibration interactions at optical frequencies has been considered by Rice *et al.*[15] and Torrance *et al.*[16] If we assume that a Holstein process holds for scattering of Drude electrons off these vibrations ($T < \theta_E$ the Einstein temperature for each molecular mode), then the one-dimensional analysis of the Holstein expression by Bright *et al.* yields the relation for the ρ_0 contribution due to molecular vibration scattering,

$$\tau_0^{-1} = 2\pi^2 \sum \gamma_\alpha \nu_\alpha, \tag{10}$$

where γ_α is the dimensionless electron-phonon coupling constant for mode α and ν_α is its frequency. Using values of γ_α calculated by Rice *et al.*[15] for $(TCNQ)^-$, we obtain $\tau_0 = 3.8 \times 10^{-15}$ sec which can be compared to the experimental values[1] of $\tau_0 \sim (3-5) \times 10^{-15}$ sec. Therefore, electron-molecular vibration scattering does not appear implausible as a contributing source to the temperature-independent term in the optical resistivity.

C. Electron-electron interaction

The pressure dependence of the conductivity is very large. In the dc case,[12-14] the conductivity increases at least by a factor of 4.5 for only a 20 kbar applied pressure ($\Delta b/b = 0.06$). This property of the conductivity is in fact most striking and must be accounted for by any theory which purports to be able to explain the source of the resistivity in these materials. The electron-electron interaction is one mechanism which has been suggested as being responsible for the observed resistivity[3,17] We consider here a simple model for the electron-electron interaction[18] in order to estimate the magnitude of the pressure dependence. For this model the conductivity is proportional to

$$\sigma \sim (B_D^4 + B_A^4)\rho_C^3 \sin^4 \tfrac{1}{2}\pi\rho_C. \tag{11}$$

In Fig. 8, we show the pressure dependence of the dc conductivity for TTF-TCNQ[12-14] and TSeF-TCNQ[14] (which by the analysis of Sec. III is directly related to the optical conductivity). There is some discrepancy between the results of Chu *et al.*[12] and Cooper *et al.*[13]; but this is not of major consequence since the important point is that the pressure dependence is large in both cases. The dashed lines in Fig. 8 show the results of Eq. (11)

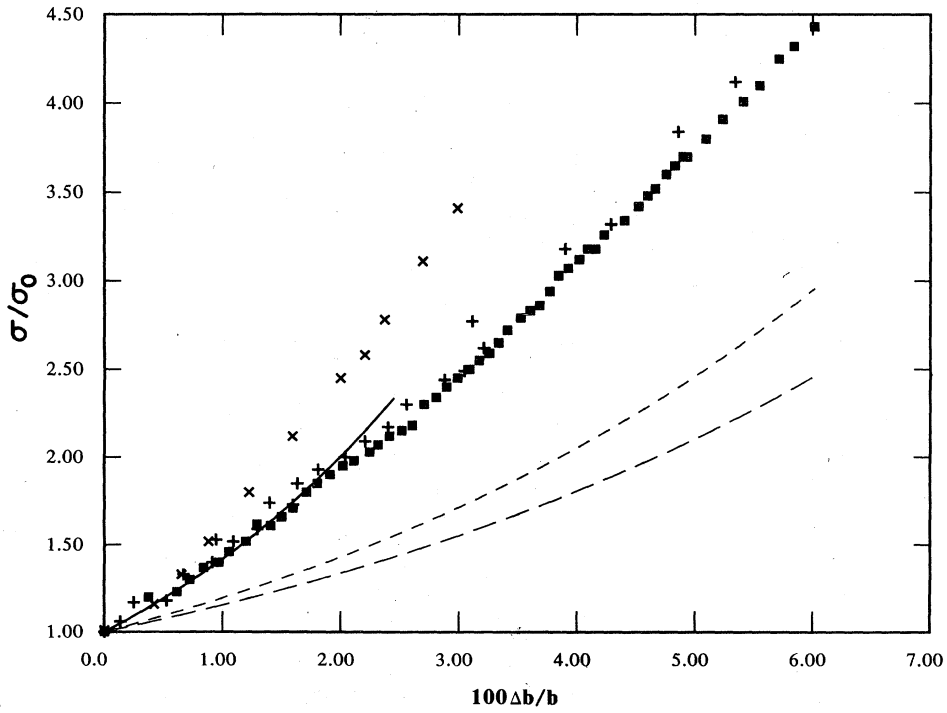

FIG. 8. Pressure dependence of the dc conductivity of TTF-TCNQ (■—Ref. 12, ×—Ref. 13) and TSeF-TCNQ (+—Ref. 14). The dashed lines show the results of Eq. (10) with constant ρ_c for both TTF-TCNQ (---) and TSeF-TCNQ (– –). The solid line is Eq. (10), for TTF-TCNQ including the change in charge transfer found from diffuse-x-ray-measurements.

for both TTF-TCNQ and TSeF-TCNQ without any pressure dependence of the charge transfer. The change in bandwidth thus accounts for a large part of the conductivity change. The discrepancy could have a number of origins. As discussed above for the plasma frequency, we have assumed Herman's results[9] for the bandwidths (Fig. 5) and a constant charge transfer. Since in this case we have only considered the region of $\Delta b/b \leq 0.06$ the bandwidths used should be satisfactory. Note however, that σ is extremely sensitive to ρ_c. Unfortunately, data on the pressure dependence of ρ_c do not exist. However, we do have a measure of ρ_c as a function of temperature from the measurements of diffuse-x-ray scattering.[19] The change in lattice parameter over the temperature range from 300 to 60 °K is equivalent to the application of 6 kbar of pressure.[20] Using the temperature dependence of the $4k_F$ reflections[21] to get ρ_c, we find a variation from 0.59 at low temperatures to 0.55 at 300 °K. Assuming this change in ρ_c is caused only by the lattice parameter variation, we insert these data into Eq. (11), and obtain the solid line in Fig. 8. The agreement with experiment is quite good.[22]

V. CONCLUSIONS

We have performed normal incidence polarized reflectance measurements on TTF-TCNQ and TSeF-TCNQ single crystals as a function of hydrostatic pressure. We can summarize our major findings and conclusions as follows.

(i) The measured plasma frequency of a segregated stack organic conductor can be separated into independent contributions from each stack. Theoretical estimates of the pressure dependence of the bandwidth of each stack can then be combined to compare with the single experimental result. We find good agreement up to about 40 kbar with the observed bandwidths, but the latter increase faster than expected thereafter.

(ii) Mathiessen's rule can be used to decompose the temperature and pressure dependencies of the optical resistivity. We observe that the temperature-independent term is also pressure independent, that is, ρ_0 is not a function of pressure to within experimental error. We conclude that the optical data, in this respect, are consistent with the dc data.

(iii) We have shown that a large part of the anomalously large pressure dependence of both the dc and optical conductivity can be interpreted within the framework of the electron-electron scattering model on the basis of changes in the stack bandwidths alone. In addition, if the change in charge transfer with temperature is taken as being equivalent to the change in transfer with pressure, theory and experiment are brought into quite good agreement.

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[10] The dashed line in Fig. 4 shows the change in plasma frequency which would be expected from inclusion of the change in charge transfer deduced from the diffuse-x-ray data (see Sec. IV). The combination of the errors in the experiment and the uncertainty in the values of the bandwith make it impossible to confirm or reject the idea of the variation of the charge transfer from Fig. 4 alone.

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[21]The exact temperature dependence is still in question since the experimental errors are quite large (see Ref. 19). Therefore, a linear interpolation between the room-temperature and 60-°K value was used.

[22]One might worry that inclusion of these lattice parameter effects might destroy the agreement with the temperature dependence of the resistivity. However, this is not the case and in fact the results are in good agreement with the approximately $T^{2.4}$ observed temperature dependence (see Ref. 18).