Deviations from Drude Response in Low-Dimensional Metals: Electrodynamics of the Metallic State of $(\mathrm{TMTSF})_2\mathrm{PF}_6$

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The optical properties of the linear chain compound bis-(tetramethyltetraselenafulvalene)hexafluorophosphate, $(\mathrm{TMTSF})_2\mathrm{PF}_6$, were examined in an extremely wide frequency range in the metallic state, above the spin density wave transition ($T > 12$ K). Parallel to the chains the conductivity has two distinct features, a zero frequency response and a finite energy absorption. Both features are temperature dependent with most of the spectral weight in the finite energy mode. Perpendicular to the chains, a Drude-like response is recovered. We discuss the implications of our findings. [S0031-9007(96)00630-8]

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There is renewed interest in the behavior of highly anisotropic conductors in their metallic state. The reason for this is twofold. First, various theories [1] based on the one-dimensional (1D) Hubbard model predict a non-Fermi-liquid state with profound implications on the spectroscopic signatures in the metallic state. The general name Luttinger liquid is used to describe the new quantum liquid state which follows from the different solutions of 1D interacting electron systems. Second, a variety of experiments [2–4] conducted on linear chain compounds with highly anisotropic electronic properties give indications of unusual features which might be signatures of such novel states of solids. Of course, real materials such as the linear-chain compounds investigated in the last two decades are not strictly one dimensional but have finite interchain coupling or interchain single particle transfer integrals. This raises interesting questions about the extent to which strictly 1D models are applicable to experiments performed on actual materials. In addition, the interplay between the periodicity of the electronic correlations and the lattice periodicity may lead to unusual features such as discommensurations and nonlinear charge and spin excitations [5,6].

In order to address these issues we have studied the optical properties of the Bechgaard salt $(\mathrm{TMTSF})_2\mathrm{PF}_6$ in a wide spectral range. The material undergoes a transition to a spin-density-wave (SDW) state at $T_{\mathrm{SDW}} = 12$ K, suggesting that the weak coupling, highly anisotropic Hubbard model is applicable to describe the properties above the phase transition. The dc conductivity is metal-like above T_{SDW} (with unusual magnetoresistance [3,4] which itself may be evidence for 1D correlations); the puzzling photoemission and nuclear magnetic relaxation experiments [2,3] were interpreted as evidence for Luttinger liquid behavior. Optical experiments performed by various groups [7–11] indicated deviations from a simple Drude picture but because of the reduced spectral ranges explored and the unavailability of large single crystals, a detailed analysis of the spectroscopic signatures was not possible and a conclusive picture of the entire frequency range was never obtained.

Using a variety of spectroscopic tools [12], we measured the optical reflectivity $R(\omega)$ with the electric field polarized both parallel ($E \parallel a$) and perpendicular ($E \parallel b'$) to the chain direction. In the submillimeter wave spectral range ($8-13$ cm^{-1}), a coherent source spectrometer based on backward wave oscillators was used. In the optical range from 15 to 10^5 cm^{-1} standard polarized reflectance measurements were performed employing four spectrometers. The data were combined with previous cavity perturbation measurements [10] in the microwave and millimeter wave spectral range. While the crystals of $(\mathrm{TMTSF})_2X$ usually appear as thin needles, we have obtained large single crystals with face dimensions up to 4×2 mm^2 in the a-b plane. The use of such crystals led to significant enhancement of the accuracy obtained for the optical reflectivity.

In Fig. 1 we display the optical absorptivity $A = 1 - R$ for both polarization directions at several temperatures. In Figs. 2 and 3 real parts of the optical conductivity and permittivity, as obtained by a Kramers-Kronig analysis of the reflectivity data, are shown for the parallel and perpendicular polarizations, respectively. For the parallel polarization direction we have chosen the low frequency extrapolation in order to meet the measured dc resistivity values. However, the dc resistivity perpendicular to the stacks [13] is in direct conflict with optical reflectivity data. A Hagen-Rubens extrapolation [14] of the 97% reflectivity observed around 10 cm^{-1} just above the transition temperature leads to a dc conductivity of 1500 $(\Omega\,\mathrm{cm})^{-1}$, significantly larger than the value 30 $(\Omega\,\mathrm{cm})^{-1}$ reported by Jacobsen *et al.* [13]. We do not know the origin of this apparent discrepancy.

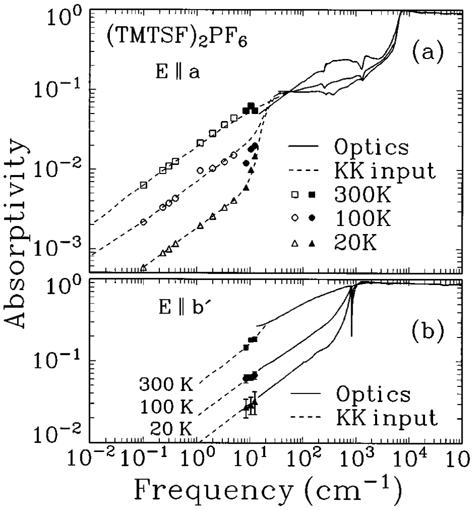

FIG. 1. Absorptivity $A = 1 - R$ of a (TMTSF)$_2$PF$_6$ single crystal as a function of frequency at several temperatures for both polarization directions, (a) parallel to the chains ($E \parallel a$) and (b) perpendicular to the chains ($E \parallel b'$). The open symbols are microwave and millimeter wave data taken from Ref. [10]; the solid symbols are results obtained with the submillimeter wave spectrometer. The solid lines are standard optical reflectivity measurements, and the dashed lines indicate the input used for the Kramers-Kronig analysis.

It is immediately evident that the optical properties are that of a highly anisotropic and well conducting material, but a Drude analysis which is in accordance with the band structure parameters does not apply: we observe neither a simple Drude roll-off nor a single plasma frequency in the direction parallel to the chains. Perpendicular to the chains a single optical feature is seen, but because of the discrepancy between the dc and high frequency data, its form is not well determined.

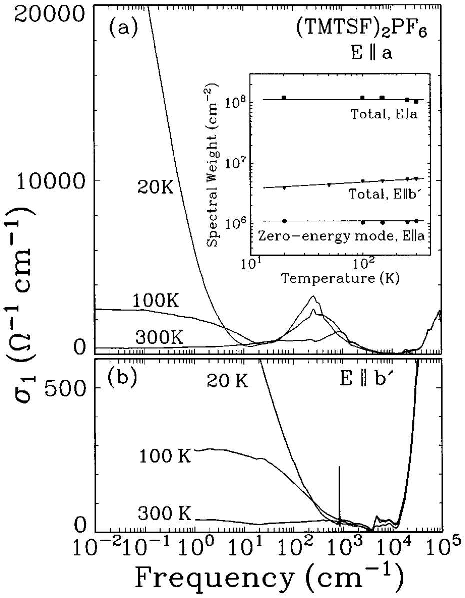

FIG. 2. Optical conductivity of a (TMTSF)$_2$PF$_6$ single crystal measured at different temperatures in both polarization directions (a) parallel and (b) perpendicular to the chains, as obtained by the Kramers-Kronig analysis of the reflectivity data. Inset shows the temperature dependence of the spectral weight $\omega_p^2(2\pi c)^{-2}$ of the total and zero energy components for $E \parallel a$ and the zero energy feature for $E \parallel b'$.

For polarization parallel to the chain direction, the optical response has two components: a zero energy (ZE) mode and a finite energy (FE) excitation, centered around 200 cm^{-1}. The combined spectral weight of the two components

$$\int \sigma_1^{\mathrm{ZE}}(\omega)\,d\omega + \int \sigma_1^{\mathrm{FE}}(\omega)\,d\omega = \frac{\pi n e^2}{2m} = \frac{\omega_p^2}{8} \qquad (1)$$

leads to a total plasma frequency $\omega_p/2\pi c = 1.1 \times 10^4$ cm^{-1} which, within experimental error, is independent of temperature [inset of Fig. 2(a)]. This value is in full agreement with the plasma frequency derived from the known electron concentration $n = 1.24 \times 10^{21}$ cm^{-3} and a band mass $m_b \approx m_e$ [15].

The zero energy mode has several unusual features. First, as the inset of Fig. 2(a) demonstrates, only approximately 1% of the total spectral weight is in this mode. This value can be calculated in two ways. Either the contribution of the finite energy mode can be subtracted from the conductivity, and the remaining zero energy mode can be integrated, giving $\omega_p^{\mathrm{ZE}}/2\pi c \approx 1.1 \times 10^3$ cm^{-1}, or the zero crossing of the dielectric constant near 25 cm^{-1} [Fig. 3(a)], when corrected for the higher frequency contributions from the finite energy mode, gives a plasma frequency of approximately 1×10^3 cm^{-1}, at all temperatures where this mode is clearly defined. It is also seen from the inset of Fig. 2(a) and Fig. 3(a) that this spectral weight is independent of temperature. Second, the measured dc conductivity of 30 000 (Ω cm)$^{-1}$ at $T = 20$ K and the expression $\sigma_{\mathrm{dc}} = ne^2\tau/m_b$ would lead to $1/2\pi c\tau = 60$ cm^{-1}. It is clear from Fig. 2(a) that the

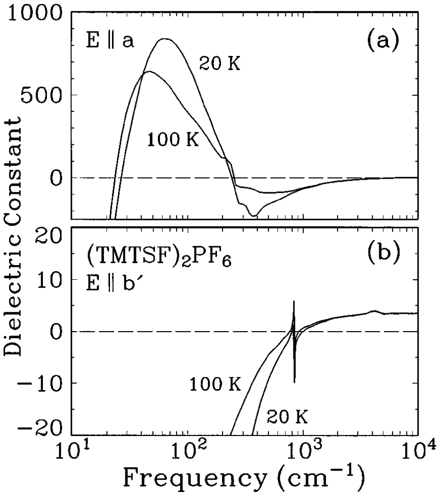

FIG. 3. The dielectric constant $\epsilon_1(\omega)$ both (a) parallel and (b) perpendicular to the chains, as obtained from the Kramers-Kronig analysis at different temperatures.

renormalized scattering rate, defined as the half-width of the Drude-like peak observed in the conductivity spectrum, is much smaller than this value. Third, the zero energy feature is well described not by a simple Drude, but by a Drude term with a frequency dependent mass and relaxation rate, $m^*(\omega)$ and $\Gamma^*(\omega)$:

$$\sigma_1^{\mathrm{ZE}}(\omega) = \frac{ne^2}{m_e} \frac{\Gamma^*}{(\Gamma^*)^2 + (\omega m^*/m_e)^2} . \qquad (2)$$

The feature around 200 cm^{-1} is also unusual. The optical conductivity measured along the chain direction is displayed on a linear frequency scale in Fig. 4. In this representation the FE structure dominates the electromagnetic response. The overall shape—the peaked structure with a pronounced asymmetry—closely resembles the spectrum of a one-dimensional semiconductor with a significant broadening, added to a flat background. Simple arguments advanced for a semiconductor with a 1D density of states (and frequency independent transition probability) lead to a square root singularity at the gap E_g, and

$$\sigma(\omega) \propto \begin{cases} 0, & \hbar\omega < E_g , \\ [\hbar\omega - E_g]^{-1/2}, & \hbar\omega > E_g . \end{cases} \qquad (3)$$

Essentially the same structure follows from the mean field solution of the density wave ground state with zero collective mode spectral weight [16], and from the solution of the 1D Hubbard model for half filling [17]. The dotted line is obtained by Eq. (3) with $E_g/hc = 200\ \mathrm{cm}^{-1}$.

For the polarization perpendicular to the chains only one component, a low frequency mode, is observed at $T > T_{\mathrm{SDW}}$, with a temperature independent spectral weight as shown in the inset of Fig. 2(a). This spectral weight yields a plasma frequency $\omega_p/2\pi c = 1800\ \mathrm{cm}^{-1}$ and, with the electron concentration given above, a band mass $m_b = 35 m_e$. This value is in full agreement with the band mass derived from band structure calculations [18]. As mentioned above, the discrepancy between these optical data and the dc data remains an open question.

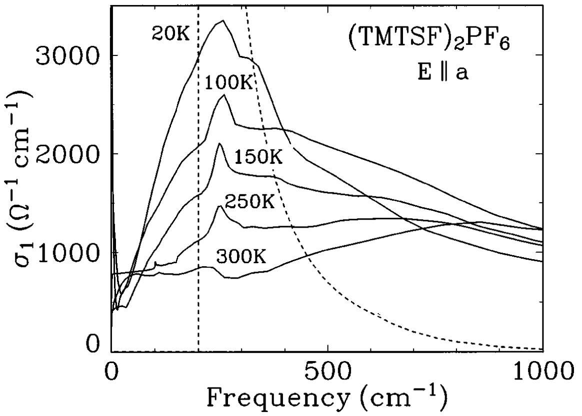

FIG. 4. The optical conductivity of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ parallel to the chains shown on a linear frequency scale at various temperatures (solid lines). The dashed line is calculated by Eq. (3) with $E_g/hc = 200\ \mathrm{cm}^{-1}$.

Next we discuss the implications of our findings. There is substantial evidence that magnetic correlations are important in the TMTSF salts [15]. At the same time, electron counting arguments together with the observed dimerization [11,15] give an electron concentration of one electron per unit cell. For a strictly one-dimensional band, the material at $T = 0$ should be an insulator in the presence of Coulomb interactions for which the Hubbard model provides an appropriate description. The metallic state observed by experiment is then due to deviations from the strictly one-dimensional half-filled band case with finite temperature effects conceivably also playing an important role. Calculations [5,6] based on the 1D Hubbard model with electron concentration close to half filling do not lead to a simple incommensurate SDW with a well defined gap at $T = 0$ and semiconducting behavior, but to a situation in which commensurate regions where the electron concentration corresponds to half filling are separated by discommensurations, leading to the appropriate overall electron concentration. The spectroscopic signatures of such a state have been calculated [5,6] and include a finite energy absorption together with a translationally invariant zero energy mode. The finite energy absorption is due to single-particle-like excitations of the half-filled regions (with features similar to those obtained for the half-filled Hubbard model) and near to half filling the zero frequency mode is due to the translationally invariant response of discommensurations. Near to half filling, the spectral weight of the finite energy excitations gives the dominant contribution to the total spectral weight with the discommensurations (with their number approaching zero as the material approaches half filling) having a small spectral weight, a feature also found here experimentally.

All the above features are qualitatively similar to those we observe, and this would argue for an interpretation where the ZE mode is due to nonlinear, translationally invariant excitations, and the feature at E_g is single particle excitations across the gap in the half-filled, commensurate regions. We note, however, one important difference between the models discussed above and the situation encountered in the $(\mathrm{TMTSF})_2X$ salts. In these materials, deviations from half filling—and hence the metalliclike low frequency conductivity—do not arise from a carrier number different from one electron per unit cell, but from two-dimensional effects which lead to significant warping of the Fermi surface. While features similar to those we have found may be explained by calculations based on a higher dimensional (as opposed to strictly 1D) half-filled correlated band, this possibility has not yet been explored theoretically. The extension of calculations from 1D to nearly 1D is essential in order to solve this aspect of the metallic behavior of low-dimensional metals.

Further experiments currently under way could help to answer the questions raised by our findings. Measurements on the $(TMTSF)_2ReO_4$ salt, which does not show dimerization, could help to establish whether such dimerization is important for the optical properties [11,19]. The extremely large dc anisotropy (significanly larger than that suggested by the anisotropy of the band structure) would suggest that the ZE mode is not of single particle origin, but is due to low-lying collective excitations. Experiments below our spectral range but at finite frequencies would be able to resolve this question.

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