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Rapid Note

Anisotropic electrodynamics of low dimensional metals: Optical studies of $(TMTSF)_2ClO_4$

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Abstract. Optical experiments are reported for the metallic state of the linear chain compound $(TMTSF)_2ClO_4$. For the electric field polarized both along the highly (a) and intermediately (b') conducting directions, a zero energy (ZE) mode and a finite energy mode (FE) are observed. The large anisotropy in the spectral weight of the FE mode is consistent with the band structure, however the spectral weight of the ZE mode is surprisingly isotropic. In the least conducting (c^*) direction, the low frequency optical conductivity along with the dc conductivity indicate the presence of a (small) Drude component only at temperatures below 10 K. These observations provide evidence for a correlation induced semimetallic state, with a 3D to 2D crossover with increasing temperature.

PACS. 78.20.-e Optical properties of bulk materials and thin films – 71.10.Pm Fermions in reduced dimensions (anyons, composite fermions, Luttinger liquid, etc.)

Fermi liquid (FL) theory has been the cornerstone of the theory of metals, and has been highly successful in accounting for the electronic properties of a wide range of materials. Recently, the breakdown of FL theory has been suggested under various circumstances. In particular, for interacting electrons in reduced dimensions theory predicts the so-called Tomonaga-Luttinger liquid (TLL) [1] for one dimensional (1D) electron systems. Several experiments [2–6], conducted on the highly anisotropic compounds, known as the Bechgaard salts [7], suggest that strong deviations from FL behavior occur in nearly 1D systems.

The Bechgaard salts are linear chain compounds based on the organic molecule tetramethyltetraselanofulvalene (TMTSF) or its sulfur analog tetramethyltetrathiafulvalene (TMTTF). Their composition is $(TMTSF)_2X$, where X is a counterion such as ClO_4, PF_6, or AsF_6. There is a charge transfer of one electron to each of the counterions. Thus the counterions have a full electronic shell while the TMTSF stack is quarter-filled. The bandwidth is anisotropic and band structure calculations lead to transfer integrals $t_a \sim 250$ meV, $t_b \sim 25$ meV, and $t_c \sim 1$ meV in the 3 crystallographic directions [8]. The anisotropy of the dc resistivities, where measured, are in broad agreement with these values, and the highest and lowest conductivities are found along the a- and c^*-directions respectively [9]. In the $(TMTSF)_2PF_6$ salt the temperature dependence of the dc conductivity, together with the results of NMR relaxation rate measurements, has been interpreted as evidence for an incipient FL at low temperature and a non-FL at high temperature [3]. The electrodynamics along the highly conducting axis shows two different excitations [5], with the high frequency behavior distinct from that of an uncorrelated 1D semiconductor and consistent with calculations based on the Tomonaga-Luttinger model of a 1D interacting electron gas. For a 1D quarter-filled band, Umklapp scattering, together with electron-electron interactions lead to the so-called Mott-Luttinger state [10]. This is an insulating state. However, an insulator-to-metal transition with increasing interchain coupling was recently established, from analysis of the optical spectra, for the Bechgaard salts [4], with $(TMTSF)_2ClO_4$ the least anisotropic and most highly conducting example of these materials.

Clearly, interchain charge excitations play an essential role in establishing a metallic state in low dimensional materials. To address this issue, we have measured the full anisotropic electrodynamics of the metallic state of $(TMTSF)_2ClO_4$. For the first time, we find two zero crossings of the dielectric function along both of the two more highly conducting directions, giving clear evidence for different types of excitations. The low energy excitation has a small spectral weight which is roughly isotropic in the a-b plane. The optical spectra also exhibit finite energy

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modes in these directions at two different energies. These observations, along with the absence of a Drude component in the c^*-axis conductivity above $T = 10$ K, are in clear qualitative disagreement with predictions based on an anisotropic FL.

Large single crystal $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ samples were grown by electrolytic methods [5,11]. The various experimental techniques, including Fourier transform infrared spectroscopy (FTIR), coherent source spectroscopy (CSS), and resonant cavity spectroscopy (RCS), which have been utilized to explore the large frequency range from the ultraviolet down to microwave frequencies, were described earlier [4,5]. The frequency dependence of the absorptivity, A ($A = 1 - R$), with R the power reflection coefficient), at several temperatures is displayed in Figure 1 for all three directions. Sufficiently thick samples for CSS and RCS measurements along the c^*-axis were not available. The fine dotted lines in the figure show interpolations and extrapolations of the data. The interpolations shown were done by hand; similar results were obtained using Drude-Lorentz data fits. The extrapolations are discussed in detail below.

At 300 K the low frequency behavior of A along the a-axis, as evaluated using FTIR, has a frequency dependence as expected for a metal in the Hagen-Rubens (HR) limit ($\omega\tau \ll 1$): $A \propto (\rho_{\mathrm{dc}}\omega)^{1/2}$, and is in agreement with the dc resistivity of $\rho_a = 1.7$ mΩcm. Along the b'-direction the low frequency response is also in accord with the HR limit and the expression for A leads to a value of $\rho_{b'}/\rho_a = 17$. The dc b'-axis resistivity has not been studied in detail, however a value of $\rho_{b'}/\rho_a \approx 20$ at 300 K has been reported [12], and it is expected that the anisotropy is somewhat less then that of the PF_6 salt for which $\rho_{b'}/\rho_a \approx 100$ [13]. Consequently, we argue that the HR limit is appropriate at $T = 300$ K for both directions. Therefore, we have normalized all the RCS and CSS data (for which the absolute values of the losses are somewhat uncertain) so that the absorptivity at $T = 300$ K agrees with the HR values.

We performed a Kramers-Kronig (KK) analysis of the absorptivities in order to obtain the complex conductivities [14]. To do this it was necessary to extrapolate the absorptivity to frequencies below the range of our measurements. For the a- and b'-axis data, this was done by assuming HR behavior for frequencies below 1 cm^{-1}. The measured dc resistivities were used to calculate HR limit values for the a-axis absorptivity. Values for the b'-axis dc resistivity were estimated by assuming that $\rho_{b'}/\rho_a = 17$ at all temperatures ($\rho_{b'}/\rho_a$ has been shown to be nearly temperature independent in the case of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ [13]). The validity of our assumptions is supported by the fact that the HR values calculated in this manner are in close agreement with the values measured at 1 cm^{-1} at all temperatures in both the a- and b'-directions. The c^*-axis absorptivity is quite high and only weakly frequency dependent, over the frequency range of the measurement. HR behavior was not observed, even at the lowest frequencies, making the low frequency extrapolation for the KK analysis uncertain. Various methods of extrapolation, including a frequency independent absorptivity, were attempted and there was little change in the resulting values obtained for the conductivity above ~ 100 cm^{-1}. The frequency dependence of the optical conductivity is shown in Figure 2, while the dielectric function is shown in Figure 3.

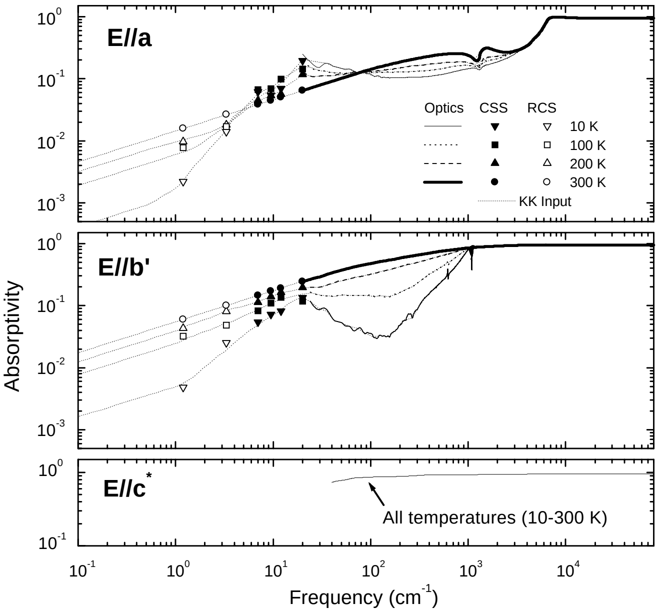

Fig. 1. The frequency dependence of the absorptivity of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ for the electric field polarized along the a-, b'-, and c^*-directions. The open and solid symbols indicate data points taken with resonant cavity measurements and coherent source spectroscopy respectively, while the solid and dashed lines indicate data taken with optical spectroscopy. The fine dotted lines show the values used for the Kramers-Kronig analysis.

First, we discuss the electrodynamics along the least conducting direction. The magnitude of the low frequency c^*-axis optical conductivity is well below the minimum metallic conductivity [15],

$$\sigma_{c^*,\min} = \frac{1}{2\hbar}\frac{e^2}{\pi}k_{\mathrm{f}}(v_c/v_{\mathrm{F}}). \tag{1}$$

With $k_{\mathrm{f}} = \pi/2a_0$, $v_a = 2t_a a_0/\hbar$, and $v_c = 2t_c c_0/\hbar$ (a_0 and c_0 are lattice constants), $\sigma_{c^*,\min}$ is about 15 $(\Omega\mathrm{cm})^{-1}$. At 100 K, the dc conductivity is about 0.5 $(\Omega\mathrm{cm})^{-1}$ [16,17], which is much smaller than both $\sigma_{c^*,\min}$ and the low frequency conductivity. This strongly suggests the complete absence of a Drude-like low frequency conductivity, at high temperatures, and indicates that the response is not that of a narrow (metallic) band, in spite of the fact that the temperature dependence of the dc resistivity in this direction follows that of the a-direction over a broad temperature range [16,17]. While this observation can be viewed as evidence for FL behavior in $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, our results strongly suggest that this is not the case. The appropriate picture may be similar to that developed for high T_{c} superconductors [18]. It has been proposed that in the absence of single-particle charge transfer between the copper oxide planes, the c-axis conductivity should have a leading order frequency dependence given by $\sigma(\omega) \propto \omega^{\alpha}$ in qualitative agreement with our experimental findings. However

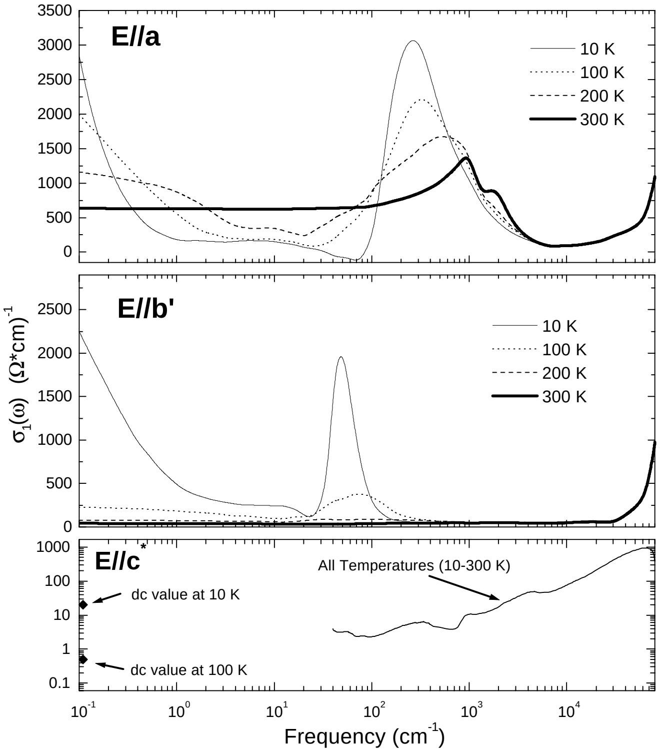

Fig. 2. The frequency dependence of the real part of the conductivity of $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ for the electric field polarized along the a-,b'-, and c^*-directions.

the value of α we find is well outside the range predicted by theory. Alternatively, the band model may break down in the c^*-direction due to thermal fluctuations, when $k_{\mathrm{B}}T$ exceeds t_c. Whichever picture applies, it is evident that $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ is a two dimensional metal above ~ 10 K. At 10 K the dc conductivity is about 20 $(\Omega\mathrm{cm})^{-1}$, which is roughly equal to $\sigma_{c^*,\mathrm{min}}$ and significantly larger than the low frequency optical conductivity, suggesting the emergence small of a Drude-like conductivity at low temperature.

We now turn to the electrodynamics observed with the electric field polarized along the highly conducting a- and b'-directions. The results at high frequencies are in broad agreement with earlier optical studies conducted over smaller spectral ranges [19]. An important feature is the observation of two zero crossings of the dielectric function along both the a- and b'-directions ($\omega_{c1}^{a,b'}$ and $\omega_{c2}^{a,b'}$; the values at $T = 10$ K are indicated by arrows in Fig. 3). This indicates the existence of two plasma frequencies, which we refer to as the upper ($\omega_{p1}^{a,b'}$) and lower ($\omega_{p2}^{a,b'}$) plasma frequencies, and therefore two types of excitations in both directions. These excitations correspond to a narrow mode centered at zero energy (ZE) and a finite energy (FE) mode peaked at 250 cm^{-1} and 50 cm^{-1} for the a- and b'-directions respectively. The values of the plasma frequency of a given mode can be determined using the expression $\omega_{pi} = \omega_{ci}\epsilon_{\mathrm{hf}i}^{1/2}$ $(i = 1, 2)$, where ω_{ci} is the frequency of the zero crossing of the dielectric function and $\epsilon_{\mathrm{hf}i}$ the "background" dielectric constant associated with higher energy modes. ϵ_{hf1} is simply given by the value of the dielectric function at the high end of our frequency range, where it is equal to about 2.5 in both the a- and b'-directions (Fig. 3 insets). ϵ_{hf2} is determined by the dielectric constant associated with the FE mode, which is given approximately by [20],

$$\epsilon_{\mathrm{hf2}} = 1 + \left(\frac{\omega_{p1}}{\omega_{\mathrm{FE}}}\right)^2 \tag{2}$$

where ω_{FE} is the position of the finite energy excitation.

This leads to a temperature independent value of $\omega_{p1}^{a} = 1.1 \times 10^4$ cm^{-1} The lower plasma frequency is 700 cm^{-1} at 10 K, and decreases somewhat with increasing temperature. For the b'-direction, two zero crossings are only observed at low temperature (Fig. 3), The plasma frequencies at 10 K in this direction are given by $\omega_{p1}^{b'} = 1600$ cm^{-1} and $\omega_{p2}^{b'} = 300$ cm^{-1}.

The spectral weight of the FE modes is related to their upper plasma frequencies by,

$$\int_{\mathrm{FE}} \sigma_1^{a,b'}\mathrm{d}\omega = \frac{\left(\omega_{p1}^{a,b'}\right)^2}{8\pi} \tag{3}$$

where the integrand is the contribution to the conductivity due to the FE mode. The spectral weight of the zero energy mode alone is given by $\frac{\left(\omega_{p2}^{a,b'}\right)^2}{8\pi}$. For both the a- and b'-directions $\omega_{p2} \ll \omega_{p1}$, indicating that the ZE mode has a vanishing spectral weight when compared with the weight associated with the FE mode [21].

Within the tight binding approximation, for the case of an open Fermi surface, the upper plasma frequencies are related to the transfer integrals by [22],

$$\left(\omega_{p1}^{a}\right)^2 = \frac{16e^2a_0^2t_a}{V_{\mathrm{m}}\hbar^2}\sin(\pi\rho/2) \tag{4}$$

$$\left(\omega_{p1}^{b}\right)^2 = \frac{8e^2b_0^2}{V_{\mathrm{m}}\hbar^2\sin(\pi\rho/2)}\frac{t_b^2}{t_a} \tag{5}$$

where V_m is the volume per molecule and ρ is the band filling factor. With $\rho = 1/4$, equations (4) and (5) lead to $t_a = 300$ meV and $t_b = 40$ meV, in close agreement with the results of band structure calculations [8].

The lower plasma frequencies, of the ZE modes differ by only about a factor of two in the a- and b'-directions [23]. This is in contrast with that expected for a simple anisotropic FL, in which they should scale with the anisotropy of the band mass: $\omega_{p2}^{a}/\omega_{p2}^{b'} = (m_{b'}/m_a)^{1/2} \approx 10$. This indicates that the spectral weight of the ZE mode is much less anisotropic than expected in the FL picture. Furthermore, it is important to note that although the value of $\sigma_{a,\mathrm{dc}}/\sigma_{b',\mathrm{dc}}$ is consistent with an anisotropic FL with isotropic scattering time, τ [24], our results suggest there is a significant anisotropy in τ since the width we find for the ZE mode is about an order of magnitude greater along the b'-direction.

Along the a-direction, the FE mode at 250 cm^{-1} resembles a somewhat smeared singularity, characteristic

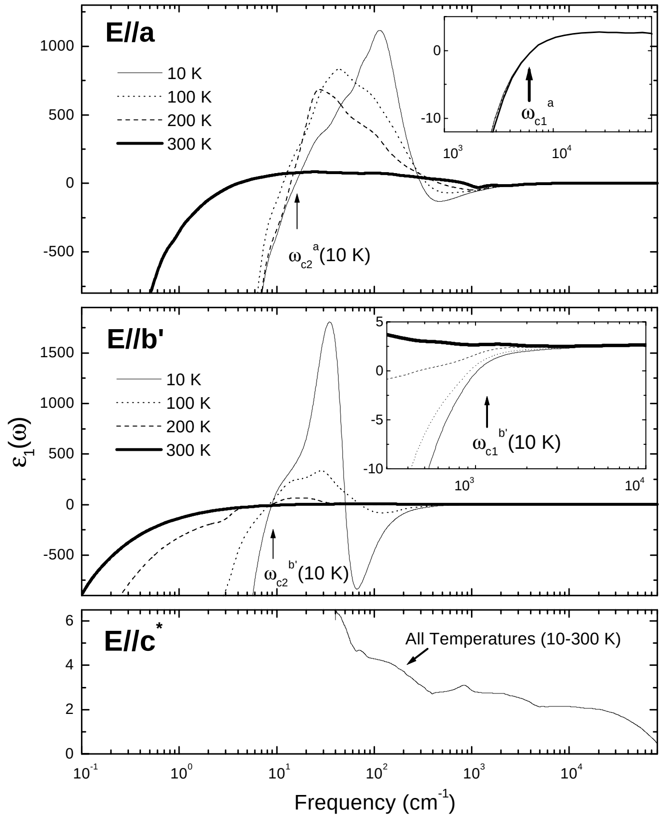

Fig. 3. The frequency dependence of the dielectric function for the electric field polarized along the a-,b'-, and c^*-directions.

of that expected for an interband transition in 1D. The density of states in one dimension leads to a conductivity near the gap given by, $\sigma_1(\omega) \sim (\hbar\omega - \Delta)^{1/2}$. At higher frequencies within a Tomonaga-Luttinger liquid scenario, a power law with a negative exponent is expected [10]. Such a description was used to account for the on-chain electrodynamics of the $(TMTSF)_2PF_6$ salt [5]. This model describes our findings for the on-chain FE mode, suggesting that this mode is due to excitations across a Mott correlation gap.

Along the b'-direction, a similar picture could also apply with the much smaller width of the absorption feature resulting from the narrower single-particle bandwidth in this direction. An alternative explanation could be that the feature is a resonance at $\omega_0 = 50$ cm^{-1} with a lifetime of $1/\tau = 35$ cm^{-1}. It remains to be seen whether this FE mode originates from an excitation across a gap or a midgap or bound state.

In conclusion, the presence of a small Drude component to the c^*-axis response at low T, along with the ZE modes in the a- and b'-directions suggests a low temperature anisotropic 3D FL state, with a small spectral weight reflecting a small number of electrons in this state. The existence of such a state would be consistent with the observation of Korringa law behavior in the NMR relaxation rate at low T [3], and with the results of early magnetoresistance studies [17]. Our observations are similar to what one would expect for a semi-metal: optical excitations at finite energies and a small pocket of electrons responsible for the dc conduction. Here however, the gap or gaps are a consequence of electron-electron interactions and Umklapp scattering. Thus we term this state a correlation induced semi-metal. How such a state emerges from a correlation induced insulator remains to be determined.

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References

1. H.J. Schulz, Int. J. Mod. Phys. B **5**, 57 (1991).
2. F. Zwick *et al.*, Phys. Rev. Lett.**79**, 3982 (1997).
3. J. Moser *et al.*, Eur. Phys. J. B **1**, 39 (1998).
4. V. Vescoli *et al.*, Science **281**, 1188 (1998).
5. A. Schwartz *et al.*, Phys. Rev. B **58**, 1261 (1998).
6. D. Jérome, C. Bourbonnais, Science **281**, 1155 (1998) and references therein.
7. D. Jérome, H.J. Schulz, Adv. Phys. **31**, 299 (1982).
8. L. Ducasse *et al.*, J. Phys. C **19**, 3895 (1986).
9. The b'- and c^*-directions, which are perpendicular to the a-direction, define the faces of the samples, and are slightly different from the b- and c-directions of the unit cell.
10. T. Giamarchi, Physica B **230-232**, 975 (1997).
11. L.K. Montgomery, in *Organic Conductors: Fundamentals and Applications*, Applied Physics Series, edited by J.P. Farges (Marcel Dekker, New York, NY, 1994), pp. 138-140.
12. K. Murata *et al.*, J. Phys. Soc. Jap. **50**, 3529 (1981).
13. G. Mihaly (private communication).
14. F. Wooten, *Optical Properties of Solids* (Academic Press, San Diego, 1972).
15. D.G. Clarke, S.P. Strong, Adv. Phys. **46**, 545 (1997).
16. L. Forró, K. Biljaković, J.R. Cooper, K. Bechgaard, Phys. Rev. B **29**, 2839 (1984).
17. J. Cooper *et al.*, Phys. Rev. B **33**, 6810 (1986).
18. P.W. Anderson, T.V. Ramakrishnan, S. Strong, D.G. Clarke, Phys. Rev. Lett. **77** 4241 (1996); P.W. Anderson, Science **256**, 1526 (1992).
19. C.S. Jacobsen, D.B. Tanner, K. Bechgaard, Phys. Rev. Lett. **46**, 1142 (1981); Phys. Rev. B **28**, 7019 (1983).
20. Equation (2) is exact for the case of a Lorentz oscillator (see Ref. [14]). Using the results of Lee *et al.* (P.A. Lee, T.M. Rice, P.W. Anderson, Solid State Commun. **14**, 703 (1974)), for interband transitions in 1D systems leads to a slightly modified expression, $\epsilon_{\mathrm{hf}} = 1 + \frac{2}{3}(\omega_{p1}/\omega_{\mathrm{FE}})^2$.
21. Y. Cao, T. Timusk, C. Bechgaard, J. Phys. I France **6**, 1719 (1996). A small spectral weight has also been inferred from these experiments. However, the spectral region where the ZE mode occurs was not covered, making the evaluation of the weight uncertain.
22. J.F. Kwak, Phys. Rev. B **26**, 4789 (1982).
23. The spectral weight of the ZE modes can also be estimated by integrating the curves in Figure 2 from zero up to a frequency somewhat greater than the width of the ZE modes. This analysis also leads to the conclusion that the spectral weight is relatively isotropic in the a-b plane. For example, integrating up to 2 cm^{-1} leads to $\omega_{p2}^{a} = 450$ cm^{-1} and $\omega_{p2}^{b'} = 430$ cm^{-1}.
24. T. Ishiguro, K. Yamji, *Organic Superconductors* (Springer-Verlag, Berlin 1990).