Unconventional Electrodynamic Response of the Quasi-One-Dimensional Organic Conductor (TMTSF)$_2$ClO$_4$

N. Cao, T. Timusk, K. Bechgaard

To cite this version:
Unconventional Electrodynamic Response of the Quasi-One-Dimensional Organic Conductor (TMTSF)$_2$ClO$_4$

N. Cao (1), T. Timusk (1,* ) and K. Bechgaard (2)

(1) Department of Physics and Astronomy, McMaster University, Hamilton, Ontario, Canada L8S 4M1
(2) Department of Solid State Physics, Risø National Laboratory, 4000 Roskilde, Denmark

(Received 18 June 1996, revised 1 August 1996, accepted 18 August 1996)

PACS.78.30.-j – Infrared and Raman spectra
PACS.75.30.Fv – Spin-density waves

Abstract. — The polarized optical reflectance of the quasi-one-dimensional organic conductor (TMTSF)$_2$ClO$_4$ has been measured along the chain axis from the far-infrared (~8 meV) to the visible (~1 eV) at temperatures between 10 and 300 K. A self-consistent description of the far infrared reflectance and the high metallic conductivity of (TMTSF)$_2$ClO$_4$ implies that a narrow mode at zero frequency carries the transport current, and there is no Drude peak corresponding to single particle motion. As the temperature is lowered below 100 K, the spectral weight of the narrow mode grows in parallel with several bands in the far infrared: a broad band with a gap-like onset at (2Δ ≈ 170 cm$^{-1}$) and several low lying phonons. These observations are consistent with a process of collective charge transport by a sliding charge density wave.

1. Introduction

It has been 24 years since Igor Schegolev introduced the organic charge transfer salts [1] to the physicists, and the passage of time has not brought forth a completely satisfactory explanation of their properties. In particular, their remarkably large electrical conductivity has been the primary subject of interest and controversy since the earliest work of Coleman et al. [2] on TTF-TCNQ. Models of collective [2,3] and single particle [4,5] transport have been proposed to explain this phenomenon. In the collective description, 1D fluctuating Fr"ohlich [6] sliding charge density waves (CDW's) carry the current. In the single particle model the organic materials are considered to be a quasi-one-dimensional metal behaving like a Fermi liquid with extraordinarily large scattering times.

The earliest evidence in support of the collective picture was the observation [7] of a discrepancy between the high dc conductivity and the low far infrared conductivity of TTF-TCNQ at low temperatures. Instead of the strong Drude peak that one would expect for a good metal, the infrared conductivity remains low, close to the 300 K value, while the dc conductivity increases by more than an order of magnitude [4] just before the phase transition into the insulating CDW state. While there is some shift of spectral weight towards low frequencies, which suggests improved metallic conductivity. a pseudogap develops in the $\sigma_1(\omega)$ spectrum [8], thus

(*) Author for correspondence (e-mail: timusk@mcmaster.ca)

© Les Éditions de Physique 1996
effectively reducing the far infrared conductivity to a very low value. The imaginary part of, $\sigma(\omega)$ shows that there is considerable spectral weight at very low frequencies below $\approx 10$ cm$^{-1}$, and this can be attributed to a collective mode [9,10]. In addition to TTF-TCNQ, these phenomena are also manifest in members of the family (X = ClO$_4$, PF$_6$, AsF$_6$) [8,9,11–15].

It is important to recognize the optical signature of this collective mode, which is superimposed upon a low conductivity single particle background. Infrared and microwave reflectance experiments show that the spectrum is characterized by a low frequency region of very high reflectance $R > 99\%$ followed by a plasma edge where the reflectance drops rapidly to the lower far infrared value of $R \approx 90\%$. In (TMTSF)$_2$PF$_6$ this edge is at $\approx 15$ cm$^{-1}$ [10,14], which implies that the plasma frequency of the narrow mode should be of the order of 1000 cm$^{-1}$. In (TMTSF)$_2$ClO$_4$ the plasma frequency of the narrow mode is even more difficult to quantify since the position of the edge, which has never been observed directly, is less than 5 cm$^{-1}$. This is the lower limit of the accurate measurements provided by Ng et al. Taking this as the upper limit of the edge we get an even lower plasma frequency for the collective mode $\approx 650$ cm$^{-1}$ [16].

In terms of the partial sum rule for the optical conductivity, the plasma frequency of the narrow mode determines the area under the conductivity curve from zero frequency to the plasma edge, provided it is well defined and the plasmons are not overdamped ($\Gamma < \omega_p$). To estimate the damping constant $\Gamma$ of the narrow mode we can, for example assume that the mode has a Drude line shape, a Lorenzian centered on zero frequency, and then find the width given by $\Gamma = \omega_p^2/4\pi\sigma$ where $\sigma$ is the dc conductivity. That this simple model is at least approximately correct is shown by the microwave data of Donovan et al. [14] which shows that the reflectance below the plasma edge follows the predicted $1 - \sqrt{\omega/2\pi\sigma(0)}$, where $\sigma(0) \approx 35 \times 10^3$ $\Omega^{-1}$ cm$^{-1}$ is close to the measured dc conductivity.

(TMTSF)$_2$ClO$_4$ is unique in that, in its relaxed state, obtained by cooling the sample slowly through its structural transition at 24 K, it remains metallic down to 1.2 K. At this point it reaches a very high conductivity before undergoing a three-dimensional superconducting transition [17]. Again, using a Drude picture for the narrow mode, its width can be estimated from the high dc conductivity to be $\approx 0.005$ cm$^{-1}$ (150 MHz) [11].

Another anomaly of the organic charge transfer salts is the temperature dependence of the dc resistivity, which is approximately quadratic in $T$. In ordinary metals, where the electron-phonon interaction dominates, the resistivity varies linearly with respect to $T$. Also between 1 and 20 K, where in conventional metals the electron-phonon interaction is frozen out, the dc resistivity of (TMTSF)$_2$ClO$_4$ shows a strong linear temperature dependence [18]. This points to a non-phonon scattering mechanism similar to what is seen in the high $T_c$ cuprates. For these materials, the linearity can be observed to very low temperatures and the resistivity curve goes through zero, instead of $\approx \Omega/4$ as one would expect for a low lying boson spectrum with a characteristic frequency $\Omega$. A large anomaly in the NMR relaxation rate for $T < 25$ K [19] and suppression of the thermal conductivity below 60 K [20,21] also suggest that a pseudogap is developing in the density of states and that collective effects may be important.

The single particle picture, on the other hand, is supported by a number of experiments in magnetic fields. For example, the observation of oscillatory phenomena in high magnetic fields [22] have generally been interpreted in terms of single particles moving in orbits [23]. The very large magneto-resistance normal to the chains in (TMTSF)$_2$ClO$_4$ is in accord with Kohler’s rule [24] which assumes that magnetic field transport effects can be characterized by $\omega_c\tau$. Since the dc resistivity $\rho$ is proportional to $1/\tau$, plots of magneto-resistance as a function of $H/\rho$ (Kohler plots) should all fall on the same curve. However one finds that Kohler’s rule is violated for transport along the chains, precisely the direction where there is anomalously high dc conductivity [25].
We now review the existing optical data. The far-infrared reflectance of relaxed (TMTSF)$_2$ClO$_4$ along the chain axis, the highly conducting direction, has been measured between 2 and 60 K for frequencies up to $\sim 200$ cm$^{-1}$ by Ng et al. [16], at 6 K to 1000 cm$^{-1}$ by Eldridge and Bates [26], and at 2 K by Challener et al. [27]. Kikuchi et al. have measured the near infrared chain-axis reflectance above 5000 cm$^{-1}$ [28]. Recently, room-temperature chain axis data have also been published by Pedron et al. from $\sim 10$ to $\sim 10000$ cm$^{-1}$ [29]. To clarify the issues of single particle vs. collective transport it is obviously important to make systematic far infrared measurements as a function of magnetic field and temperature. While some data exist in magnetic fields they are limited in temperature and frequency coverage, focussing mainly on the temperature dependence of low lying features [16,27,30-32].

There is considerable variation in the available data, both in terms of the magnitude of the reflectance and in the presence and absence of phonon features. Some of this variation can be attributed to thermal cycling of samples, which tends to reduce the strength of phonons, and incorrect Kramers-Kronig extrapolations to high frequencies. Irradiation by defects has also been reported to reduce the magnitude of phonon peaks. Most of the measurements are supposed to be in the relaxed state, but there is a possibility that some of the samples were not fully annealed.

With improved reflectance techniques, infrared groups are now able to obtain the optical properties of difficult samples to a high degree of reproducibility [33,34]. Thus we are now ready to complete the measurements of the chain-axis reflectance of (TMTSF)$_2$ClO$_4$ in the missing frequency range from $\sim 60$ to $\sim 8000$ cm$^{-1}$ over a larger range of temperatures. In this paper we report on some preliminary measurements.

2. Experimental Results

Single crystals $3.0 \times 0.5 \times 0.2$ mm$^3$ in the $a$, $b$, and $c$ directions respectively, were assembled into a mosaic of five crystals with the $ab$ plane facing the incident radiation. The sample was cooled slowly below 40 K ($\sim 1$ K /min) to reach the relaxed state of the anion order-disorder phase transition at 24 K [35]. An in situ evaporation technique was used to correct any errors due to the roughness of the surface [33].

Figure 1 shows the chain axis reflectance at 300, 200, 100, and 10 K. Our room-temperature data are quite similar to those given by Pedron et al. except for a few percent magnitude difference [29], and the high frequency data are in agreement with Kikuchi et al. [28]. Above 150 cm$^{-1}$, our data match well with the reflectance reported by Challener et al., but these authors show a dip in reflectance down to 80% below this frequency; a dip not seen by other investigators. In contrast, Eldridge and Bates [26] show a reflectance that roughly agrees with ours in the same region but drops to 70% above 150 cm$^{-1}$ The magnitude of the 10 K reflectance in the present study matches the data point of Ng et al. at 60 cm$^{-1}$ [16]. It should be noted that the measurements were done by focussing the radiation on a sample with toroidal mirrors whereas Ng et al. employed an immersion cryostat with light pipe optics. In both cases an overcoating technique was used to correct for diffraction effects from the irregular surface.

The variation in the reflectance of (TMTSF)$_2$ClO$_4$ as measured by different groups is larger than can be attributed to variations in experimental techniques. The variation cannot be due to the use of small samples and mosaics since the metallic overcoating technique effectively eliminates such errors, for it gives reflectance values that are accurate to better than one percent [33]. This has been checked in simple systems where the reflectance can be calculated from dc conductivity and Drude theory. Stainless steel is a good system with an absolute reflectance similar to the samples under study here.
Another plausible explanation for the variation is the presence of a surface layer of a different composition than that of the sample. The variation in the thickness of the layer could then be a variable that affects the measured reflectance. However, it is difficult to see what material would produce the observed effects. A simple dielectric on top of a metal has little influence in the far infrared. This can be justified by examining the effects of ice, which often shows up in systems with inadequate vacuum trapping, as a band around 3200 cm\(^{-1}\), provided that the ice is present in thicknesses greater than a few hundred angstroms. On a metallic surface the far infrared ice lines are not visible, even if the thickness is enough to bring the reflectance at 3200 cm\(^{-1}\) down by 50%. Simulations with the known optical constants of ice agree with these observations [36].

To extract the real and imaginary parts of \(\sigma(\omega)\), by Kramers-Kronig analysis, the data must be extrapolated outside the range of measured reflectance. At high frequency, we extended our data between 8000 and 25000 by using the room-temperature data of Kikuchi et al. [28], a constant value between 25000 and 10\(^6\) cm\(^{-1}\), and free electron behaviour \((R(\omega) \propto \omega^{-4})\) beyond 10\(^6\) cm\(^{-1}\). Since the low frequency limit of our measurements was 60 cm\(^{-1}\) we used the data of Ng et al. [16] on the low-frequency side down to \(\sim 5\) cm\(^{-1}\). To do the lowest frequency extrapolation, the parameters of the narrow mode must first be estimated. The following procedure was used: We assumed that the mode had a Drude shape, and fit the measured reflectance to a narrow peak with a plasma frequency \(\omega_{pn}\) and width \(\gamma_n\) using the known dc conductivity. The 10 K values found from the fit were 634 and 0.034 cm\(^{-1}\), respectively. A series of Lorentz oscillators was used to represent the rest of the infrared conductivity. Figure 2 shows the fitted reflectance as the solid curve. We then used this fitted reflectance in the 0 to 5 cm\(^{-1}\) region as the lowest frequency extension in the Kramers-Kronig analysis of \(R(\omega)\). Other assumptions for the plasma frequency of the narrow mode do not affect the overall \(\sigma(\omega)\) in the region of actually measured data \(\omega > 5\) cm\(^{-1}\) but the amplitude of the low frequency phonon line is strongly affected by the strength of the assumed low frequency mode. This is illustrated in Figure 3 where the other choices for the plasma frequency shown in Figure 2 are used in the KK extrapolation to calculate the conductivity.
Fig. 2. — The measured low frequency reflectance (the solid line), and the fitted low frequency extensions (all the data below 5 cm\(^{-1}\)) The sharp plasma edges below 4 cm\(^{-1}\) are caused by a narrow mode at low frequency.

Fig. 3. — The calculated low frequency conductivity with different extensions to low frequency as shown in Figure 2. The solid line uses a low frequency extension from a least squared fit to the measured reflectivity.

The real part of \(\sigma(\omega)\) for \((\text{TMTSF})_2\text{ClO}_4\) along the chain axis in the far-infrared is shown in Figure 4. The corresponding values of the dc conductivity [17] are also shown. In accord with all previous data on this system, the far infrared \(\sigma(\omega)\) is quite small in contrast with the much larger dc conductivity [17]. There is no sign of Drude absorption, instead the optical
conductivity is dominated by a very broad band, with $\sigma(\omega)$ increasing with frequency. As the temperature is lowered below 100 K, the spectral weight of the phonon modes grows and there is an overall shift of spectral weight to lower frequencies. A gap develops in the broad band below 170 cm$^{-1}$ ($2\Delta \simeq 21$ meV). The reflectance fitting procedure, described above shows that the spectral weight of the narrow mode as well as that of the phonons grow as the temperature is lowered.

3. Discussion

In discussing the data it is imperative to address the question of the existence of the narrow mode since we do not obtain it directly from the real part of $\sigma(\omega)$. It has been suggested that the anomalous reflectance of the organic conductors can be accounted for by a "broken strand" model, where the conducting chains are broken into segments of finite length by defects and cracks [37]. However, experiments performed on (TMTSF)$_2$PF$_6$ [13,38] have revealed that it has high reflectance at microwave frequencies which is associated with the narrow mode component of the conductivity. As a surface with defects and cracks should have lower reflectance at lower frequencies, the above mentioned observations would negate any suggestion that imperfections are responsible for the anomalous reflectance.
The presence of the narrow mode is also evident in the reflectance edge seen by Jacobsen et al. in the far infrared reflectance of (TMTSF)$_2$PF$_6$ (Ref. [10], Fig. 16). Jacobsen et al. estimate, from the spectral weight of the narrow mode, a plasma frequency of 900 cm$^{-1}$, whereas analysis of the recent microwave data of Dressel et al. [15] gives a plasma frequency of 1100 cm$^{-1}$. It can be seen from the good agreement of these data that the so-called gap between the microwave and the infrared has been bridged and both sets of measurements support the concept of a narrow mode of low spectral weight as the charge carrier in (TMTSF)$_2$PF$_6$.

To conclude, we note that the absence of Drude absorption and a spectral weight consistent with the carrier concentration in the $a$ direction, (and in the $b$ direction [16]) shows that single particle transport is diffusive in all directions and at all temperatures. The reason for the high conductivity, in the chain direction is a narrow mode of large mass accompanied by a gap of the order of 170 cm$^{-1}$ in a relatively low conductivity single particle band. These observations, along with the observation of the growth of phonon lines, are in accord with predictions for the conductivity spectrum in the presence of sliding charge density wave transport [39].

We finally return, briefly, to the question of reconciling these observations with the overwhelming evidence in support of band transport by single particles, as seen in a variety of magnetotransport experiments in high fields. It is clear that the answer lies in careful reflectance measurements in high fields - measurements that would map out the phase boundary between the CDW zero field region and field region where the CDW is destroyed and single particle transport becomes effective.

Acknowledgments

We would like to acknowledge C. Bourbonnais, V. Emery, D. Jérome and J. Musfeldt for valuable discussions, R. A. Duncan and G. Hewitson for technical support. This work was funded by the Natural Science and Engineering Research Council of Canada (NSERC) and by the Canadian Institute for Advanced Research, (CIAR).

References


