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The Far-Infrared Properties of $(TMTSF)_2Pf_g$ and $(TMTSF)_2ClO_4$ at 6K

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THE FAR-INFRARED PROPERTIES OF $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ AT 6K.

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Abstract The far-infrared reflectivities of $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$, as well as TTF-TCNQ, has been obtained by a "composite-bolometer" technique, in which a small doped-germanium bolometer is attached to the rear face of a single organic crystal. The temperature rise of the crystal, upon irradiation, is proportional to 1-R, which leads to accurate values of R when it is very close to unity. The conductivity for $(TMTSF)_2PF_6$ at 6K for $\vec{E} \| \vec{a}$ has an asymmetric response with a peak at 45 ± 5 cm^{-1}, in fair agreement with the thermal gap of 33 cm^{-1}, and a sharp feature at 18 ± 1 cm^{-1}. For $\vec{E} \| \vec{b}$ the response follows the inverse square-root dependence very well, and the peak is at 35 ± 5 cm^{-1}. The TTF-TCNQ response also shows a one-dimensional type behaviour with a peak at 300 cm^{-1}. The $(TMTSF)_2ClO_4$ results are compared with other data.

INTRODUCTION

The far-infrared conductivity expected for one-dimensional conductors with charge-density or spin-density waves have been considered by Lee, Rice and Anderson[1], and recently by Fenton and Psaltakis.[2] Fig. 1 shows the insulating phase in which one expects an energy gap 2Δ above which the single particle conductivity is an asymmetric peak with an inverse square-root singularity. The C.D.W. or S.D.W. is pinned and is optically-active in the gap.

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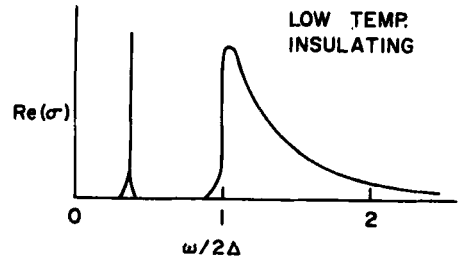

FIGURE 1 Conductivity versus frequency for an incommensurate CDW system.

EXPERIMENT AND RESULTS

Far-infrared measurments in this field have so far been mainly of reflectivity, R, from an aligned mosaic of single crystals[3,4], since the crystals are small, and the absorption too high for transmission studies. These are, however, difficult to calibrate and there are problems with diffraction effects. On the other hand we have had some success with a bolometric method for TTF-TCNQ[5], in which the crystal acts as its own detector. At liquid helium tempratures it is a semiconductor with a reasonable resistance and temperature coefficient of resistance. The d.c. conductivity of $(TMTSF)_2PF_6$ is, however, always too large for this method, and so we constructed instead a "composite-bolometer" in which a small doped-germanium bolometer is attached to the rear face of the crystal (see Fig. 2), which directly measures the temperature rise, ΔT, of the sample upon irradiation. The crystal and bolometer are supported by the electrical leads. The absorption coefficient is so large that no radiation is transmitted and ΔT is proportional to 1-R. When R is high, say 0.97, then a 10% accuracy in 1-R is equivalent to a required 0.3% accuracy in R. Fig. 2 shows a light guide with straight sides to preserve the polarization. A cone of microwave absorber after the bolometer reduces the radiation striking the Ge bolometer directly. The spectrum can be easily corrected for this small amount of "leakage" radiation by subtracting the spectrum obtained when the radiation is dropped at a high frequency, 140 Hz, say. The Ge

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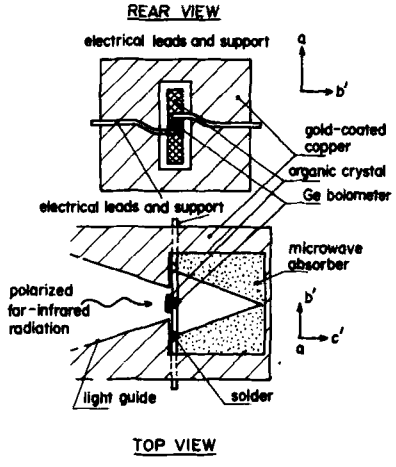

FIGURE 2 Two views of the composite bolometer, which is cooled to 6K, along with a load resistor.

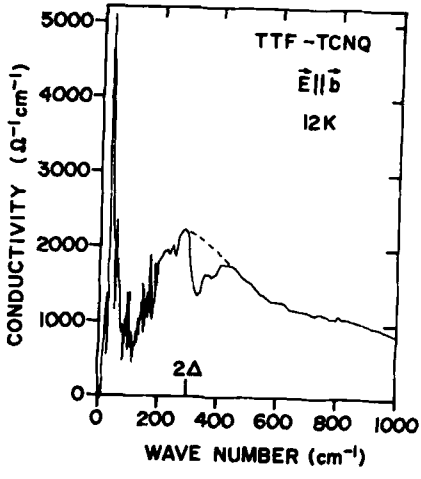

FIGURE 3 Conductivity of TTF-TCNQ obtained by both simple bolometer and a composite bolometer techniques.

bolometer is fast and its response approximately constant up to several hundred hertz. The crystal composite, however, is slow because of its large heat capacity and low thermal conductance through the crystal and glue, so that its response is inversely proportional to the chopping frequency. A low frequency between 5 and 10 Hz was required to obtain the sample spectrum.[6] At high frequencies, the crystal composite response was negligible. The sample spectra were ratioed with background spectra taken with a Golay detector, which has an almost flat response throughout our wavenumber region.

A first check of the method was made with a composite of TTF-TCNQ. The results were identical to those obtained using the crystal as a simple bolometer.[7] Fig. 3 shows the conductivity, which may be seen to resemble the theoretical prediction of Fig. 1, having an asymmetric peak at the measured energy gap of 300 cm^{-1} and a pinned C.D.W. at 40 cm^{-1}. The structure below the dashed line is due to an intramolecular mode of TCNQ, $\nu_9(a_g)$, with well-known strong electron-phonon coupling.

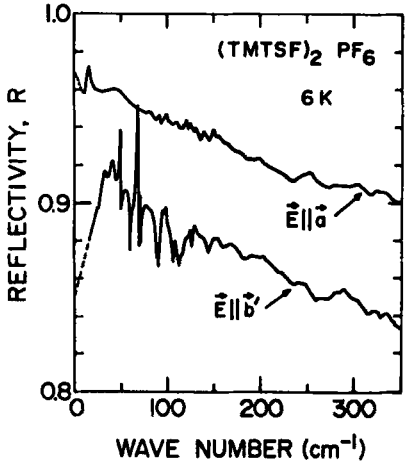

FIGURE 4. Polarized reflectivity of $(TMTSF)_2PF_6$ obtained by a composite bolometer technique.

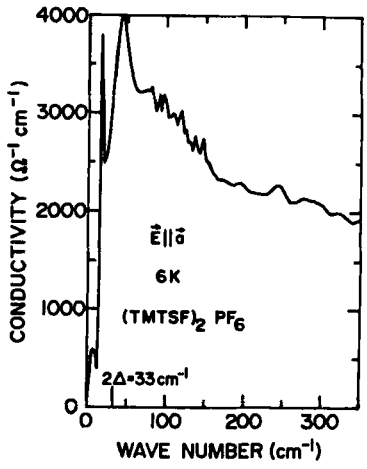

FIGURE 5. The conductivity obtained from a KK analysis of the $\vec{E} \parallel \vec{a}$ reflectivity in Fig. 4.

Fig. 4 shows the low-energy reflectivity spectra obtained for $(TMTSF)_2PF_6$ in the insulating S.D.W. state. These have been calibrated by matching our $\vec{E} \parallel \vec{b}$ value at 950 cm^{-1} to that obtained by Jacobsen et al.[4] at 25K. A Kramers Kronig analysis was performed

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using the data of Jacobsen et al.[8] between 1000 and 12,000 cm^{-1}. Above 12,000 cm^{-1}, R was assumed constant. Below 10 cm^{-1} R was extrapolated as shown. Fig.'s 5 and 6 show the conductivities obtained. Both show an asymmetric peak. For $\vec{E} \| \vec{a}$, the peak position is 45 ± 5 cm^{-1}, slightly higher than the thermal gap of 33 cm^{-1} measured by Chaiken et al.[9] It is also flatter than the inverse square root dependence expected. These features may be a result of the slight two-dimensionality. For $\vec{E} \| \vec{b}'$, on the other hand, the inverse square-root dependence holds well and the peak position of 35 ± 5 cm^{-1} agrees with the thermal gap. It is not completely understood why this polarization appears so one-dimensional.

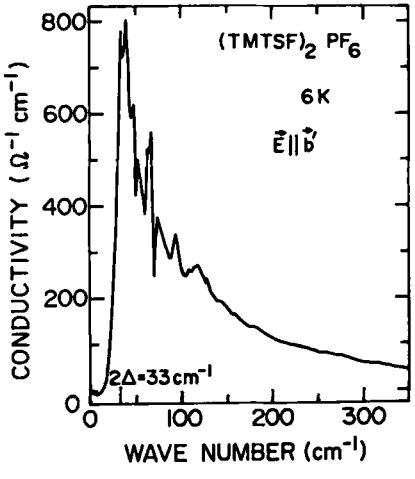

FIGURE 6. The transverse conductivity obtained from a KK analysis of the reflectivity in Fig. 4

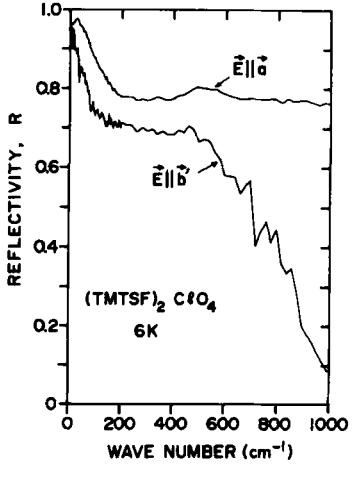

FIGURE 7. Polarized reflectivity of thermally-cycled $(TMTSF)_2ClO_4$ using the composite-bolometer method.

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For $\vec{E} \| \vec{a}$ a sharp peak at 18 cm^{-1} is also observed, the nature of which is presently unknown. Preliminary temperature-dependent results[10] indicate that it is still present at 15K, above the SDW transition, so that it is unlikely to be the pinned SDW, or zero-field anti-ferromagnetic resonance (magnon). This is probably in the microwave region, as observed by Gruner[11]. For $\vec{E} \| \vec{b}'$, there are several sharp lattice modes below 100 cm^{-1}, which we have investigated in powder spectra.[6] As with TTF-TCNQ, no strong mode at 300 cm^{-1} for $\vec{E} \| \vec{a}$, as reported by Tanner et al.,[4] has been observed.

Finally, we tried to reproduce the results of Timusk[3] on $(TMTSF)_2ClO_4$ with our technique. Unfortunately the only data we presently have is from a crystal which has been thermally cycled many times, and this probably explains the few discrepancies. Fig. 7 shows the reflectivities and Fig. 8 the resulting conductivities up to 1000 cm^{-1}. $(TMTSF)_2ClO_4$ is still a metal at 6K and so the behaviour of Fig. 1 is not expected. Fig. 8 shows the

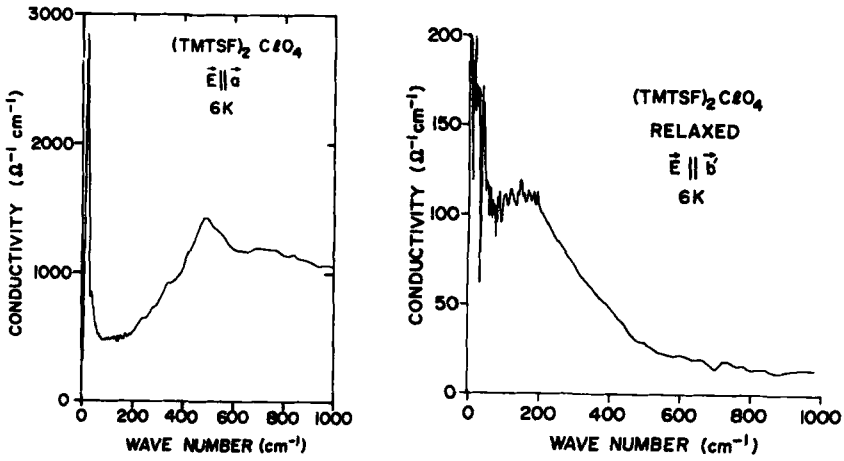

FIGURE 8. The polarized conductivities of a thermally cycled sample of $(TMTSF)_2ClO_4$ obtained from a KK analysis of Fig. 7

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expected rising conductivity due to the Holstein process for $\vec{E} \| \vec{a}$ but there is also a strong peak at 20 cm^{-1}. The $\vec{E} \| \vec{b}'$ polarization, on the other hand, shows a spectrum similar to that expected for the insulating phase. Fig. 9 compares our results with those of Timusk. For $\vec{E} \| \vec{b}'$ the agreement is excellent both in magnitude and shape. The only obvious effect of quenching is to considerably broaden the phonon antiresonance at 30 cm^{-1}, and other vibrational features. For $\vec{E} \| \vec{a}$, the cycling has presumably removed the sharp 7 cm^{-1} feature and surface deterioration has lowered the reflectivity, which has reduced the conductivity between 50 and 200 cm^{-1}. Otherwise there is fair agreement. There is an obvious similarity between the 18 cm^{-1} feature in the PF_6 compound and the 25 cm^{-1}, or possibly the 7 cm^{-1}, feature in the relaxed ClO_4.

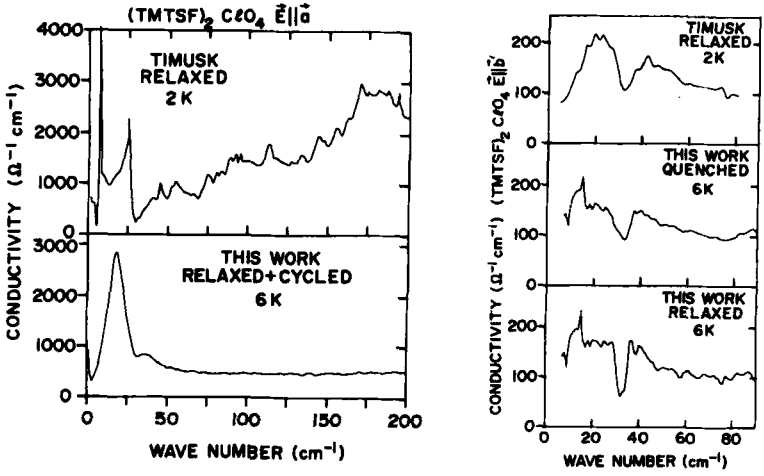

FIGURE 9. A comparison of the low-energy portion of our conductivity spectra of thermally-cycled $(TMTSF)_2ClO_4$ with those of Timusk (Ref. 3).

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