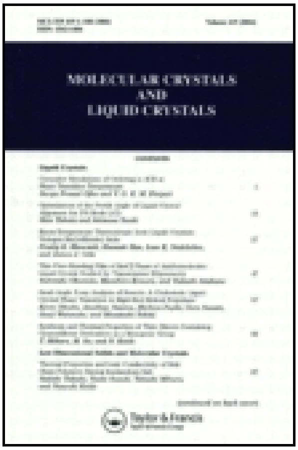

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Far-Infrared Studies of Di-Tetramethyltetr Aselenafulvalium Salts

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FAR-INFRARED STUDIES OF DI-TETRAMETHYLTETRASELENAFULVALIUM SALTS

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Abstract A detailed far-infrared study of two TMTSF compounds, ClO_4 and SbF_6 is presented. In the metallic state, the overall conductivity $\sigma_1(\omega)$ can be characterized by two relaxation times, a very long lifetime $\tau_c(>10^{-11}s)$ associated with the dc conductivity and a frequency dependent scattering time τ_p due to phonons. The first lifetime is associated with the 'zero frequency mode' which has an effective mass M* of 250-650 m* while the second is due to Holstein volume process. In the spin density wave state, gaps of 20 cm^{-1} and 180 cm^{-1} were observed for the ClO_4 and SbF_6 compounds respectively.

INTRODUCTION

Over the past few years we have been studying the far-infrared properties of the $(TMTSF)_2X$ compounds.[1,2] In this paper, we report on the results of two of the compounds measured, the ClO_4 and SbF_6 salts. The ClO_4 compound was studied both in the relaxed-state and quenched-states[3] while the SbF_6 salt was studied above and below the metal-insulator (MI) transition temperature ≈ 12K. The more insulating states of both compounds have been identified as a spin density (SDW) states via electron spin resonance.[4,5]

The organic charge transfer salts are unusual in several aspects. At ambient pressure, the materials change to a SDW state rather than charge density wave (CDW) state as observed in other organic materials. Perhaps, the most interesting feature is the high dc conductivity at low temperatures. We will present results in this paper that throw some light on the nature of the mode responsible for the high dc conductivity and also, discuss the mechanism that produces the absorption at higher frequencies.

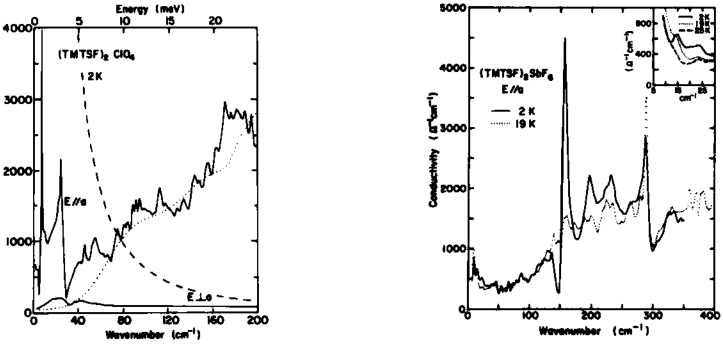
EXPERIMENTAL

All the measurements were done at ambient pressure on crystals arranged in the form of a mosaic. The details of the ClO_4 compound experiments have been presented earlier.[2] For the SbF_6 salt, two sets of crystals from the same batch with approximately 10 single crystals in one and 8 in another were studied. The absolute reflectance was measured.[2] The details of the experimental technique and extrapolations used in Kramers-Kronig transformations have been described elsewhere.[2]

RESULTS AND DISCUSSION

(a) Holstein Conductivity

The overall conductivity is shown in Figs. 1 and 2 for the ClO_4 and SbF_6 compounds respectively. In the metallic state the conductivity profile is characterized by an initial rise in $\sigma_1(\omega)$ before levelling off at about 200 cm^{-1} for both compounds. This behaviour is typical of Holstein volume absorption[6-8] a process where a photon is absorbed with a simultaneous creation of electron-hole pair and a phonon. The minimum energy is the phonon energy. We will fit the conductivity using eqn. (29) ref. 8 where we ignore scattering by impurities. The function $\alpha^2_{tr}(\omega)F(\omega)$ (eqn. (30), ref. 8) is the phonon density of states weighted by the square of the e-p coupling for transport. In our calculations, we shall model the function by Gaussian peaks. Three broad peaks centred at 70, 130 and 350 cm^{-1} with full width at half-maximum (FWHM) of 40, 40 and 100 cm^{-1} respectively were taken. These peaks were chosen to represent the librational, bending and stretching modes of these materials. Two sharp peaks at 173 and



FIGURES 1 & 2 Real part of the conductivity for $(TMTSF)_2ClO_4$ and SbF_6 respectively. Dashed line (Fig. 1) is the Drude conductivity with $\Gamma = 3.5$ cm^{-1} and dotted line is the Holstein fit. Fig. 2 (dashed line) is the Holstein fit.

256 cm^{-1} with FWHM of 10 cm^{-1} were used to simulate the internal TMTSF modes.[9,10] The amplitudes of the peaks were, in order of increasing frequency, 0.09, 0.3, 2.5, 2.5 and 0.18 respectively for the ClO_4 salt. For the SbF_6 salt, the amplitudes were reduced by a constant factor (0.55/0.95) to reflect the lower $\sigma_1(\omega)$. Fig. 1 (dotted line) and Fig. 2 (dashed line) shows that the overall fit is very satisfactory.

One can estimate the total strength of the e-p coupling for transport via

$$\lambda_{tr} = 2\int d\omega/\omega \; \alpha^2_{tr}(\omega)F(\omega) \qquad (1)$$

This gives λ_{tr} of 0.95 for ClO_4 and 0.55 for SbF_6 salt. The values of λ_{tr} are very reasonable and give additional support to the Holstein process. However, the values depend on the accuracy of the fit and on the shape of the assumed $\alpha^2_{tr}(\omega)F(\omega)$. The observed oscillator strength of the continous absorption that we associate with the Holstein process is over 95% of 1/8 ω_p^2.

(b) Zero Frequency Mode

The inset of Fig. 2 for 25K shows a rise in conductivity as $\omega \to 0$ that may be evidence of the zero frequency mode associated with the high $\gtrsim 20000\ (\Omega.\mathrm{cm})^{-1}$ dc conductivity. There is a shift of oscillator strength to higher frequencies as the temperature was lowered. This is possibly due to the pinning of the zero frequency mode at a finite frequency. In Fig. 1 for the $\mathrm{ClO_4}$ compound, we did not see any evidence of the zero frequency mode. If we assume a Drude model with dc conductivity of $500000\ (\Omega.\mathrm{cm})^{-1}$, then the half-width is $3.5\ \mathrm{cm}^{-1}$ (dashed line, Fig. 1). Clearly the mode is much narrower than this and our observed conductivity does not follow the single particle Drude model.

An estimate of the lifetime τ_c of the zero frequency mode[11,12] of the $\mathrm{ClO_4}$ salt can be obtained by using the measured dc conductivity and the oscillator strength of the zero frequency mode Ω_p^2 since

$$\sigma_{dc} = \Omega_p^2\ \tau_c\ 1/4\pi \qquad (2)$$

A value of Ω_p can be obtained from $\varepsilon_1(\omega)$. Fig. 3 shows that $\varepsilon_1(\omega)$ first crosses zero at $\simeq 18\ \mathrm{cm}^{-1}$ and levels off at $\varepsilon_H \simeq 500$. Since $\varepsilon_1(\omega) = \varepsilon_H - (\Omega_p/\omega)^2 = 0$ at $\omega = 18\ \mathrm{cm}^{-1}$, $\Omega_p = 400\ \mathrm{cm}^{-1}$. This gives $\tau_c \simeq 1.0 \times 10^{-9}\mathrm{s}$ ($\Gamma_c \simeq 0.005\ \mathrm{cm}^{-1}$) for 2K. This value is to be compared to the single particle value. Similarly, for the $\mathrm{SbF_6}$ compound, $\tau_c = 1.7 \times 10^{-11}\mathrm{s}$ ($0.32\ \mathrm{cm}^{-1}$) in the metallic state i.e. 25K. The half-width for the $\mathrm{ClO_4}$ salt at 25K is $\simeq 0.09\ \mathrm{cm}^{-1}$, more than three times narrower. This may explain why the 'tail' of the zero frequency mode is visible in $\mathrm{SbF_6}$ and not in $\mathrm{ClO_4}$.

The effective mass M* of the zero frequency mode can be calculated from

$$\Omega_p^2 = 4\pi n e^2/M^* = \omega_p^2 m^*/M^* \qquad (3)$$

Using the plasma frequencies from Jacobsen[13] et al. M* = 646 m* for the $\mathrm{ClO_4}$ salt. Table 1 summarized the particulars of the zero frequency mode.

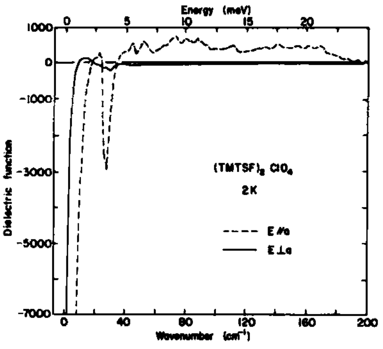


FIGURE 3 Real part of the dielectric constant for $(TMTSF)_2ClO_4$. For E||a, ε_1 first crosses zero at 18 cm^{-1} and levels off at ≃ 500.

TABLE 1 Zero frequency mode parameters

Material	T(K)	τ_c(s) [$\Gamma(cm^{-1})$]	M*(m*)
$(TMTSF)_2ClO_4$	2	1.0×10^{-9} [0.005]	646
$(TMTSF)_2SbF_6$	25	1.7×10^{-11} [0.32]	273

We have also studied the effect of a magnetic field applied in the b-c plane on the zero frequency mode. No observable broadening was seen with fields up to 0.7 Tesla. This is in contradiction with the idea that the huge transverse magnetoresistance is due to scattering to those parts of the Fermi surface with higher scattering rate as in the single particle picture.[14]

(c) Phase Phonons in the SDW State

In Fig. 2 we observed that as the sample undergoes a transition to a SDW state three sharp lines appeared. The strength and position as a function of temperature are shown in Fig. 4. There is a decrease in intensity as the temperature increases and also a shift to a higher frequency for peak A'. This peak can be identified from Raman scattering[9] to be $a_g\nu_7$ mode of the TMTSF molecules with frequency 173 cm^{-1} that has been shifted down to e-p coupling.

(Bozio[10] et al. assigned this mode to $a_g\nu_{12}$ with a value of 146 cm^{-1}.) Peak C' would then correspond to $a_g\nu_{11}$ with a calculated frequency 240 cm^{-1}. A plot of the integrated normalized intensity of peak A' versus temperature (Fig. 5 solid circles) shows an abrupt rise for T<14K. The shift in frequency of peak A' versus temperature also shows rapid change below 14K. (Fig. 5, open circles.)

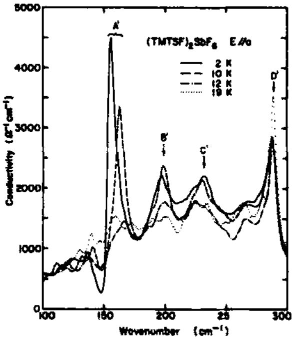


FIGURE 4 Temperature dependence of lines A', B' and C'.

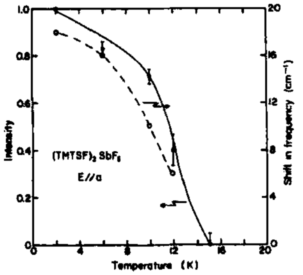
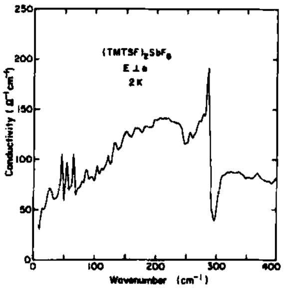


FIGURE 5 Plot of normalized intensity versus temperature for A', and shift in frequency versus temperature.

Strong absorptive lines have been observed in the CDW state in TEA-$(TCNQ)_2$.[15] These lines were interpreted as phase phonons. Our system, however, is in the SDW state and phase phonons have not been reported in this state. Nevertheless, we will use the theory by Rice[16] to fit our observation. The theory predicts the phase phonons can be observed along the chain direction and not perpendicular to it. This is consistent with our observation (Fig. 6). The persistence of the high conductivity below 200 cm^{-1} implies a partial presence of a metallic state. In $(TMTSF)_2PF_6$, SDW was shown to coexist with a metallic state via nuclear magnetic resonance.[17] To use Rice's theory one needs to subtract the free-electron conductivity from the total conductivity. The free-electron conductivity is non-Drude and difficult to calculate theoretically. Consequently we shall subtract the free-electron conductivity from $\sigma(2K)$ by multiplying $\sigma(19K)$ by a constant factor i.e. $\sigma_{SDW} = \sigma(2K) - X\sigma(19K)$ where X was chosen to be 0.75. Fig. 7 (solid lines) shows the resulting SDW conductivity. The threshold at $\simeq 180\ cm^{-1}$ is identified as the onset of single particle excitations across a SDW gap, $2\Delta_{SDW}$.



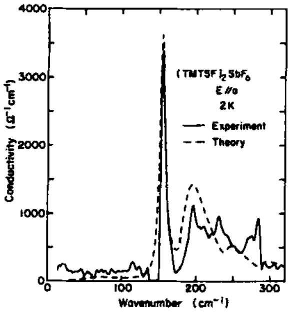


FIGURE 6 $\sigma_1(\omega)$ for $(TMTSF)_2SbF_6$ in the E⊥a direction.

FIGURE 7 The SDW part of $\sigma_1(\omega)$ of $(TMTSF)_2SbF_6$ at 2K and theoretical fit.

Fig. 7 (dashed line) shows the conductivity found using eqn. (5) ref. 15. The total e-p coupling, λ was estimated to be 0.22 from mean field theory in the tight binding approximation,[18] $2\Delta_{SDW} = 8E_F[-1/\lambda]$ where $E_F = 0.276$ eV.[19] This value of λ is smaller than λ_{tr} since λ is summed over the gapped part of the Fermi surface rather than over the whole Fermi surface. Table 2 lists the parameters used in the fit. The width of the lines was assumed to be $12\ cm^{-1}$ and the total oscillator strength to be 6% of 1/8 ω_p^2. The hypothetical gap value, 2V, (i.e. without the e-p coupling) is taken to be $150\ cm^{-1}$ from which the static dielectric constant $\varepsilon_s = 1+(\omega_p^2/2\Delta_{SDW})^2[2/3+\lambda\Delta_{SDW}/V]$ (eqn. 6 ref. 15) for the SDW part was calculated to be 2900. A similar value was obtained by subtracting $\varepsilon_1(2K)$. There are ten other higher intermolecular modes and they were arbitrarily assigned as one line with $\omega = 500\ \text{cm}^{-1}$, $\Gamma = 50\ \text{cm}^{-1}$ and e-p coupling 0.03. Intermolecular modes which couple to the electrons were given as one line of frequency $70\ \text{cm}^{-1}$, $\Gamma = 50\ \text{cm}^{-1}$ and e-p coupling 0.1.

TABLE 2 Parameters used in Fig. 7 (dashed line)

Mode	Frequency $\omega_n(\text{cm}^{-1})$	Fitted λ_n
$a_g\nu_{11}$	240	0.01
$a_g\nu_{12}$	173	0.07
SbF_6 line?	288	0.01

It is natural to extend the phase phonons argument to interpret the sharp lines at 7 and 25 cm^{-1} observed in the ClO_4 compound (Fig. 2). However, the phase phonons explanation is difficult to justify for the following reasons: First, the lines were observed up to ≈ 60K.[2] If there is any phase transition at such high temperatures, then it should be seen in other measurements e.g. dc conductivity which would have a MI transition in the 60K region. No such transition was observed. Second, phase phonons originate from symmetric modes. Group theory calculations[20] show that there is no symmetric mode in this frequency region. Third, there is an abrupt shift down by 2 cm^{-1} for the higher frequency peak as the sample was heated above 24K.[2] This temperature is associated with the anion order/disorder. Thus it would appear that the ClO_4 anions do play a part, at least in the 25 cm^{-1} peak. Fourth, the 25 cm^{-1} peak is magnetic field dependent whereas no field dependence was observed in the SbF_6 compound. Lastly, a similar temperature dependence in the $E\perp a$ direction, albeit different in peak position, and a shift at 24K strongly implies the observed features are not phase phonons.

(d) SDW Gap

For the SbF_6 salt, the SDW gap $(2\Delta_{SDW}/k_BT_{SDW} \simeq 18\text{-}21$ where $T_{SDW} = 12\text{-}14K)$ is too large to be described within mean field theory which gives a BCS-type[18] ratio, $2\Delta/k_BT_{mf} = 3.5$. However, when fluctuation effects are included this ratio will change. For example, in an incommensurate Peierls transition,[21] $T_{mf} = 4T_{CDW}$ giving $2\Delta/k_BT_{CDW} = 14$.

In the Q-state of the ClO_4 salt, the reflectance shows a minimum at 14 cm^{-1}. The corresponding conductivity displays an asymmetric peak with a threshold at 20 cm^{-1} (Fig. 8) that can be identified as a SDW gap. This follows from the first two terms of eqn. (5) ref. 15. There are other factors that suggest that the peak is due to single particle excitation across a SDW gap. It disappears by 7K i.e. above the SDW transition temperature. No magnetic field dependence was observed.

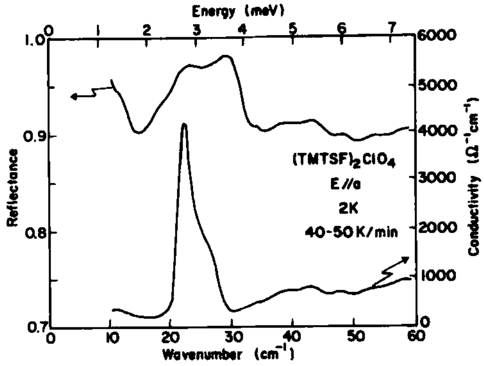


FIGURE 8 Reflectance and corresponding $\sigma_1(\omega)$ of $(TMTSF)_2ClO_4$ when cooled at a rate of 40-50 K/min from $\simeq$ 70K.

The SDW transition temperature for the ClO_4 salt depends on the rate of cooling[22] and is $\simeq$ 3.5-6.5K. Taking T_{SDW} to be 5K, gives $2\Delta_{SDW}/k_BT_{SDW} = 5.8$, a value much smaller than the SbF_6 salt. It is not clear as to why there is such a vast difference in the ratio for the two compounds.

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