

Far-infrared spectrum of di-tetramethyltetraselenafulvalene hexafluoroarsenate [(TMTSF)₂AsF₆]

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New results are presented on the far-infrared properties of the quasi-one-dimensional compound di-tetramethyltetraselenafulvalene hexafluoroarsenate [(TMTSF)₂AsF₆] below the spin-density-wave (SDW) transition temperature. The infrared conductivity is reduced at frequencies below 60 cm⁻¹ but we do not observe a well-developed energy gap. A 5-cm⁻¹-wide mode centered at zero frequency can be observed with a strength that is consistent with the freezing out of carriers below the SDW transition as observed by dc conductivity. There is no evidence of high metallic single-particle conductivity in our measurements above the transition temperature in the conducting state. A strong continuous absorption in the 50–500-cm⁻¹ region can be seen and we associate it with a Holstein absorption with a λ_{tr} of 0.6, a value that is consistent with the temperature dependence of the dc conductivity.

INTRODUCTION

The far-infrared conductivity of quasi-one-dimensional organic conductors presents a puzzle. In view of the very high dc conductivity observed in these materials, one is led to expect a metallic high reflectivity in the far infrared. What is generally observed, however, is a substantial absorption of energy in the (5–100)-cm⁻¹ range. There is no evidence of the strong metallic reflectivity expected for a material with a high single-particle conductivity. Kramers-Kronig analysis shows that the absorption is a result of a very sharp mode of low oscillator strength at the origin.^{1–5} The mode exists up to a temperature of the order of 50–100 K, well above the spin-density-wave transitions in the di-tetramethyltetraselenafulvalene [(TMTSF)₂] compounds. Thus one is led to conclude that the narrow mode is responsible for the high dc conductivity in these materials and that the conductivity is due to a collective mode of low oscillator strength and large mass.

There is plenty of evidence that one-dimensional order is important in these materials. Superlattice reflections seen by x-ray diffraction, antiferromagnetism, etc., all point to the existence of charge- (CDW's) and spin-density (SDW's) waves at low temperature. It was noted by Barden⁶ and by Lee *et al.*⁷ that charge-density waves could carry a current, and that in the absence of pinning the relaxation time associated with this current was the phonon lifetime rather than the much shorter electron lifetime. Zettl *et al.*⁸ report on measurements of collective response due to SDW's in the microwave region for di-TMSF hexafluorophosphate [(TMTSF)₂PF₆] below the transition temperature 11.5 K.

The view that collective transport can exist well above the transition temperature is more controversial. Nevertheless, the far-infrared data point in the direction of a sharp low-frequency mode, strongly coupled to the lattice. Tanner *et al.*³ show that in (TMTSF)₂PF₆ at 100 K the low-frequency conductivity (at 10 cm⁻¹) is only some 400 (Ω cm)⁻¹, whereas the dc conductivity at this temperature is of the order of 3000 (Ω cm)⁻¹. In tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) the narrow mode can be seen above the CDW transition temperature at 160 K, and it is particularly well developed² at 60 K with a half-width of 4 cm⁻¹, a width that is inconsistent with the dc conductivity in the single-particle picture.

On the other hand, many measurements, particularly various forms of magnetotransport measurements, can best be interpreted in terms of a high single-particle conductivity in the metallic state. The evidence for this point of view has been summarized by Thomas *et al.*⁹ for TTF-TCNQ and recently by Greene and Chaikin¹⁰ for the TMTSF salts. The idea is that these materials are simply very good conductors where the current is carried by a conventional single-particle mechanism with a very long relaxation time.

An attempt has been made by Weger and Kahve,¹¹ to reconcile these contradictory observations in terms of a picture with a damaged surface layer, the broken-strand model. Since the penetration depth of the far-infrared radiation is only of the order of a micrometer, the measured properties are very sensitive to possible surface alterations. In the model the surface layer that is seen by the far-infrared radiation is assumed to be of lower conductivity than the bulk that is responsible for the dc conductivity

measured with the four-probe technique. The lowered conductivity is caused by breaks in the conducting chains, and with a suitable choice of parameters a region of depressed far-infrared conductivity that agrees with observation can be obtained.¹²

In this paper we would like to report on far-infrared conductivity measurements on di-TMTSF hexafluoroarsenate [(TMTSF)₂AsF₆]. This compound has been fairly extensively studied with other techniques. The material undergoes a metal-insulator (*M-I*) transition at 12 K under ambient pressure as measured by dc conductivity.^{13,14} Below this temperature it exhibits semiconducting behavior with an activation energy of 14.5 cm⁻¹. At a pressure of about 10.5 kbar, a superconducting state was observed at ≈1 K. Bechgaard and co-workers¹⁵ and Torrance *et al.*¹⁶ showed that the semiconducting state was antiferromagnetic in nature, possibly a SDW state. In many aspects, the AsF₆ salt is similar to (TMTSF)₂PF₆ material. The material has a well-developed plasma resonance at 10 000 cm⁻¹ for light polarized in the conducting direction.¹⁷ Measurements normal to this direction show no evidence of a plasma edge, particularly in the least conductive direction, along the *c* axis.

Previous measurements of the far-infrared properties of (TMTSF)₂AsF₆ have been in the conducting state. In this paper we would like to extend the measurements to the SDW state and to present data both above and below the transition temperature, and with particular emphasis on the observations at very low frequencies below the 100-cm⁻¹ region, where the tail of the mode responsible for the dc conductivity is expected to dominate the spectrum.

RESULTS

The measurements were done with Fourier-transform spectroscopy. A mosaic consisting of eight single crystals was studied. The crystals had a shiny black surface and were mounted with strain-gauge glue on a mica ring so

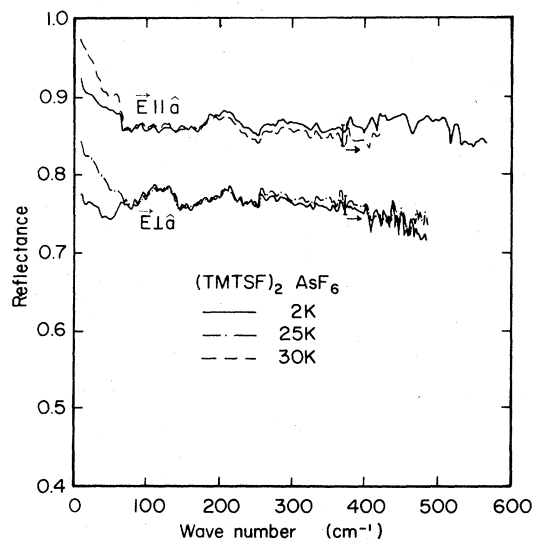


FIG. 1. Far-infrared reflectance of (TMTSF)₂AsF₆. The dashed curves are for the highly conducting state and the solid curves for the insulating SDW state.

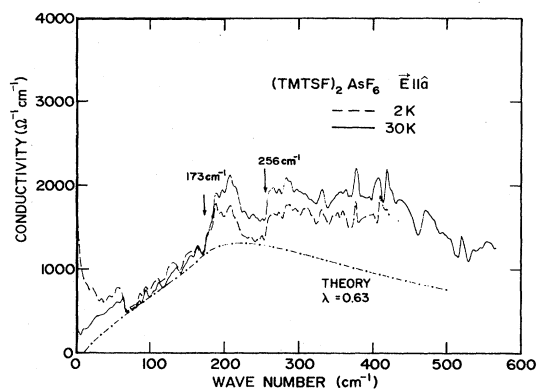


FIG. 2. The frequency-dependent conductivity of (TMTSF)₂AsF₆ in the chain direction. The features pointed to with arrows correspond to internal modes of the TMTSF molecule. The dotted curve is a calculated contribution to the conductivity from the Holstein phonon emission with a λ_{tr} of 0.63.

that a flat optical surface was obtained. The uncorrected reflectance was about 65%. We feel that the low reflectance is caused mainly by remaining gaps and irregularities of the surface of the mosaic. All the data were taken under ambient pressure. A more detailed description of the method is given elsewhere.¹⁸

In Fig. 1 we show the overall reflectance in the spectral region 8–550 cm⁻¹ for $E \parallel \hat{a}$ and $E \perp \hat{a}$. The most significant feature is the decrease in reflectance below ≈63 cm⁻¹ as the temperature was decreased from 25 to 2 K past the magnetic ordering temperature at 12 K. The reflectance is higher for $\omega > 200$ cm⁻¹ at 2 K than at 30 K. Our reflectance values at high frequency in the *a* direction match to within 1% those of Jacobsen *et al.*¹⁷ In Fig. 2 we show the conductivity for $E \parallel \hat{a}$ obtained with Kramers-Kronig transformations. There are two broad peaks with thresholds at 173 and 256 cm⁻¹. We associate these tentatively with the $a_g \nu_{12}$ and $a_g \nu_{11}$ modes, respectively, of the TMTSF molecules. A similar threshold at ≈167 cm⁻¹ is also observed in (TMTSF)₂ClO₄.⁴ Above 350 cm⁻¹ the level of uncertainty does not permit positive

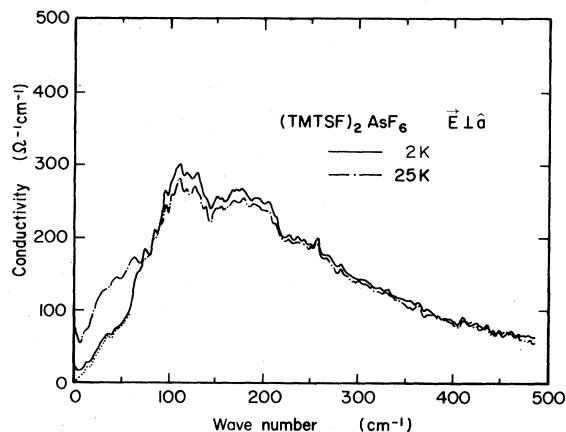


FIG. 3. Frequency-dependent conductivity in the direction perpendicular to the conducting axis. The decreased conductivity at low frequency and low temperature is evidence of a SDW gap. The dotted line corresponds to an alternate extrapolation to zero frequency.

identification of any particular modes. The conductivity perpendicular to the *a* direction is displayed in Fig. 3. Its overall level is about an order of magnitude smaller than that in the *a* direction. There is a dramatic decrease in conductivity below 60 cm⁻¹ upon entering the SDW state.

The temperature dependence of the low-frequency conductivity is shown in Fig. 4. What seems to be unique in this material is the temperature dependence of the conductivity below 65 cm⁻¹. Below the *M-I* transition the conductivity is dominated by a peak of about 5 cm⁻¹ half-width centered on zero frequency. The extrapolated dc value of this conductivity peak agrees with the measured dc conductivity.¹⁶ At 2 K the correct dc value can only be obtained by extrapolating to 94% reflectivity instead of to unity at $\omega=0$, consistent with the idea that the material undergoes a complete metal-to-semiconducting transition. However, our data show that while the low-frequency optical conductivity decreases when the material goes into the insulating state, even at the lowest temperatures there is no true gap in the optical conductivity. In this, the AsF₆ material resembles the SbF₆ reported on previously.¹⁹

Above 30 K the low-frequency extrapolation of the far-infrared conductivity seems to level off at 300 (Ω cm)⁻¹, whereas the dc conductivity approaches 20 000 (Ω cm)⁻¹. This behavior parallels other one-dimensional organic conductors and implies the existence of a very narrow mode at zero frequency below the region of sensitivity of our equipment.

DISCUSSION

The increase and leveling off in the real part of the conductivity $\sigma_1(\omega)$ is characteristic of Holstein conductivity.²⁰⁻²³ In the Holstein volume process, a photon is absorbed, with the simultaneous creation of an electron-hole pair and a phonon. The threshold energy is the phonon energy ω_0 , and as the phonons are exhausted, $\sigma_1(\omega)$ levels off. The conductivity is given by

$$\sigma_1(\omega) = \omega_p^2 \tau / 4\pi(1 + \omega^2(\tau^*)^2),$$

where

$$\frac{1}{\tau} = (2\pi/\omega_0) \int_0^{\omega_0} d\omega (\omega_0 - \omega) \alpha_{tr}^2(\omega) F(\omega)$$

and

$$\tau^* = \tau(1 + \lambda_{tr}),$$

where λ_{tr} is the total strength of the electron-phonon coupling for transport and is given by

$$\lambda_{tr} = 2 \int \frac{d\omega}{\omega} \alpha^2 F(\omega).$$

The function $\alpha_{tr}^2(\omega)F(\omega)$ is the phonon density of states weighted by the square of the electron-phonon coupling for transport. We use a simple Debye spectrum with a cutoff frequency of 160 cm⁻¹ to model $\alpha_{tr}^2(\omega)F(\omega)$. In Fig. 2 (dotted line) we show that a satisfactory fit to the conductivity is obtained with a λ_{tr} of 0.6±0.2. The overall conductivity fit could be improved if sharp optical modes were included in the spectrum, but it is not possible to do this without disturbing the amplitude at low fre-

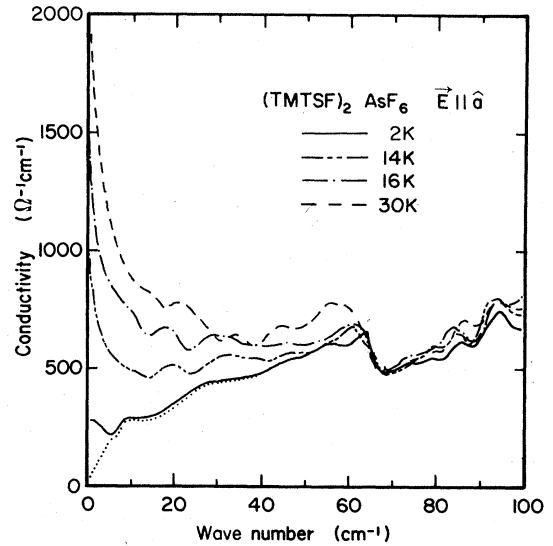


FIG. 4. Temperature dependence of the low-frequency conductivity in the chain direction. The material undergoes a *M-I* transition at 12 K, and below this temperature the conductivity is dominated by a peak, centered at zero frequency, whose amplitude agrees well with the measured dc conductivity. Above the transition temperature the dc conductivity approaches 20 000 (Ω cm)⁻¹, while the optical conductivity remains low. This discrepancy can be interpreted in terms of a very narrow mode at the origin.

quencies, since any added high-frequency modes increase the overall λ_{tr} and reduce the conductivity. We should, however, point out that the value of λ_{tr} depends on the overall magnitude of the conductivity obtained from the Kramers-Kronig analysis and on the shape of the fitted $\alpha^2 F$ spectrum.

In a pure metal, scattering by phonons plays a dominant part in the dc resistivity. A standard formula for the resistivity²⁴ is

$$\rho = \frac{4\pi}{\omega_p^2} \int_0^{\infty} \frac{\beta \alpha_{tr}^2 F(\omega) d\omega}{(e^{\beta\omega} - 1)(1 - e^{-\beta\omega})},$$

where $\beta = \hbar\omega/kT$. The dc resistivity obtained from the $\alpha^2 F$ this way is shown in Fig. 5. Typical measured resistivities^{16,25} are also shown. We note that the calculated values are slightly lower than the measured resistivity in the temperature range from 100 to 300 K, a discrepancy that could result from geometrical obstructions to the current flow such as cracks and other defects. Under these conditions the measured resistivity would be multiplied by a temperature-independent factor. The overall temperature dependence is in reasonably good agreement with the experimentally observed T^2 dependence, except that at higher temperatures the assumed Debye spectrum for the phonons has a tendency to depress resistivity. An allowance for thermal expansion and inclusion of higher-frequency phonons will make the calculated curve approach closer to the observed T^2 dependence. It is evident from the (TMTSF)₂ClO₄ curve, however, that the electron-phonon interaction of the form used here will not

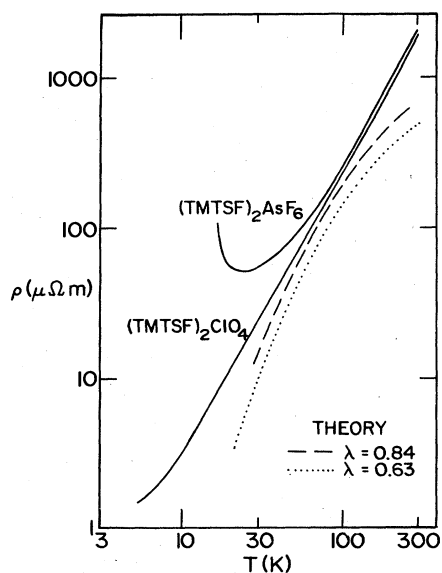


FIG. 5. Temperature dependence of the electrical resistivity calculated from the $\alpha^2(\omega)F(\omega)$ used to fit the infrared data—dashed curve. Solid curves are the observed resistivities taken from the literature, Ref. 16 for the AsF_6 salt and Ref. 25 for the ClO_4 compound.

explain the low-temperature (2–15 K) resistivity in this material.

The most important discrepancy that remains between the observations and the interpretation in terms of single-particle theory is the very low conductivity observed at low frequencies in the conducting state above the M - I transition temperature, much lower than the measured dc conductivity, a discrepancy observed in most one-dimensional materials. Below the M - I transition there is no discrepancy: Our data are consistent with the dc measurements and with the idea of an insulating state where a few carriers remain above the gap with a relaxation time of the order of 5 cm^{-1} . The conductivity decays as these carriers freeze out.

There are two possible interpretations of the low far-infrared conductivity above the M - I transition. If the far-infrared measurements are correct (that is, the observed reflectance and the calculated conductivity represent the bulk properties of the material), then the measurements imply the existence of a very narrow zero-

frequency mode of very large effective mass.

In this picture the effective mass of the zero-frequency mode can be estimated by fitting the data with a damped oscillator at zero frequency.^{2,5,26} The real part of the dielectric constant is given by

$$\epsilon_1(\omega) = \epsilon_H - (\Omega_p/\omega)^2,$$

where ω_H is the high-frequency dielectric constant, which, from our Kramers-Kronig analysis, is about 500, and Ω_p is the collective-mode plasma frequency, which turns out to be 400 cm^{-1} . The conductivity is given by

$$\alpha_{\text{dc}} = \Omega_p^2 \tau / 4\pi. \quad (1)$$

Using a dc conductivity of $20000 (\Omega \text{ cm})^{-1}$ characteristic of the metallic state above the M - I transition at 30 K, we obtain a width of 0.34 cm^{-1} or 10 GHz for the zero-frequency mode. The effective mass of the mode is $270 m_e$. Below the transition temperature the mode is presumably pinned with a small enough pinning potential to keep it below 5 cm^{-1} , the lower limit of our measurements. Measurements of the ac conductivity of $(\text{TMTSF})_2\text{AsF}_6$,¹³ and in $(\text{TMTSF})_2\text{PF}_6$ (Ref. 27) at 25 GHz, in contrast, show a conductivity that is very similar to the dc value. An application of the single-particle formula for the lifetime of the mode

$$1/\tau = \omega_p^2 / 4\pi\sigma$$

gives, at 12 K with $\sigma = 20000 (\Omega \text{ cm})^{-1}$ and $\omega_p = 10000$, a value for $1/\tau = 55 \text{ cm}^{-1}$. Such a broad peak would dominate the far-infrared spectrum, giving a high reflectivity of the order of 98% up to a frequency of 40 cm^{-1} . The essential feature of the collective mode, the large effective mass, is a direct consequence of its low oscillator strength, which, in turn, rises from the lack of metal-like reflectivity in the $(10\text{--}100)\text{-cm}^{-1}$ region.

The second interpretation of the low-frequency data above the M - I transition in terms of the damaged surface layer, as suggested by Weger and Kahve,¹¹ and the reflectivity measured at the lowest frequencies, is not characteristic of the bulk and is depressed. At this stage the far-infrared experiments cannot distinguish between the two models.

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