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Far-infrared reflectivity of bis-tetramethyltetraselenafulvalene hexafluoroarsenate $[(\mathrm{TMTSF})_2\mathrm{AsF}_6]$ through the spin-density-wave phase transition

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Measurements are presented of the ratio of the far-infrared reflectivity of a crystal mosaic of bis-tetramethyltetraselenafulvalene hexafluoroarsenate $[(\mathrm{TMTSF})_2\mathrm{AsF}_6]$ above and below the spin-density-wave phase transition at 12 K. Using the already published 6-K reflectivity spectra measured by a composite-bolometer technique, the higher-temperature reflectivity spectra are obtained. For radiation polarized perpendicular to the conducting axis, the reflectivity shows a sharp increase if the temperature is raised through 12 K. The resulting conductivity shows a disappearance of the semiconducting gap and its replacement by a normal metallic conductivity. For radiation polarized parallel to the conducting stacks, on the other hand, a small decrease in reflectivity is observed. The resulting conductivity shows a persistent gap in the metallic state with a reduced peak near 70 cm^{-1}. These data are further evidence for a collective mode at zero frequency at temperatures well above the phase transition.

I. INTRODUCTION

The existence of collective transport in pseudo-one-dimensional organic conductors in their metallic state is still controversial. Arguments supporting it have been presented by Jerome,[1] in which he contends that well-developed cooperative phenomena, due to fluctuations, can exist up to 30 K in the highly conducting $(\mathrm{TMTSF})_2X$ salts where TMTSF represents tetramethyltetraselenafulvalene. Except for the salt with the ClO_4^- anion, these materials undergo a metal-insulator phase transition at low temperatures. In particular the salts with octahedral anions such as PF_6^-, AsF_6^-, and SbF_6^- have a 12-K phase transition with the formation of a spin-density wave (SDW). The dc conductivity above the transition is very high [$\sim 100\,000\ (\Omega\,\mathrm{cm})^{-1}$ in the PF_6 compound], and this is thought to be due to a cooperative phenomenon such as a sliding SDW. Greene and Chaikin,[2] on the other hand, argue that the materials are merely exceptionally good conductors in which the current is carried by conventional single particles, with very little scattering.

Of course the first organic conductor to be considered as a collective conductor was tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ). The arguments for and against contributions to the peak conductivity near 60 K arising from a sliding charge-density wave (CDW) were summarized in two adjacent articles by Cohen *et al.*[3] and Thomas *et al.*[4] in 1976. Subsequently dc measurements[5] under pressure showed a drop at commensurability, which would pin the CDW and most recently dc measurements[6] have shown nonlinear effects under high electric fields, in the temperature range in which only the TCNQ chain is distorted. Both results support the theory of a current-carrying CDW.

The measurement of the far-infrared reflectivity should discriminate between the two models. A normal metal has a high reflectivity, due to the high conductivity, continuing through the infrared until the plasma frequency is approached. Results obtained by Tanner, Cummings, and Jacobsen[7] for TTF-TCNQ, however, showed a low conductivity in the metallic state in the far-infrared region. Their data support the existence of a zero-frequency collective mode with a width of 4 cm^{-1}. A similar conclusion was reached by Jacobsen *et al.*[8] for $(\mathrm{TMTSF})_2\mathrm{PF}_6$ and by Ng *et al.*[9–11] for $(\mathrm{TMTSF})_2\mathrm{ClO}_4$, $(\mathrm{TMTSF})_2\mathrm{SbF}_6$, and $(\mathrm{TMTSF})_2\mathrm{AsF}_6$. In these cases a mode with a width of only 0.3 cm^{-1} (10 GHz) is proposed. Unfortunately, measurements on $(\mathrm{TMTSF})_2\mathrm{PF}_6$ in the microwave region up to 35 GHz by Javadi *et al.*[12] show little sign of such a feature.

With considerable evidence in favor of a single-particle approach, Marianer, Kaveh, and Weger[13] proposed a "broken-strand" model, which together with a phonon-drag theory, can successfully reproduce the far-infrared results. They suggest that the low conductivity below $\sim 200\ \mathrm{cm}^{-1}$ results from phonon drag, while a damaged surface layer affects the conductivity between 200 and 1000 cm^{-1}, since the penetration depth decreases with frequency.

Our previous far-infrared results for TTF-TCNQ (Refs. 14 and 15), $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (Ref. 16), $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ (Ref. 16), $(\mathrm{TMTSF})_2\mathrm{SbF}_6$ (Ref. 17), and $(\mathrm{TMTSF})_2\mathrm{AsF}_6$ (Ref. 17) have all been in the semiconducting phase. This is because we have employed a low-temperature bolometric technique to obtain the reflectivity R. Either the crystals themselves were used as the bolometer, in the case of TTF-TCNQ,[15] or a "composite" was made by fastening a small germanium bolometer to the rear face of the crystals.[16,17] In either case, if the absorption is high then the measured signal is proportional to $1-R$. The results we obtained with this method agreed in part with those obtained by the more usual method of reflecting from a crystal mosaic, but disagreed in other important respects. In particular, we find values of R approaching 98% in the far-infrared region, with the polarization along the highly conducting direction. Our most accurate result was obtained for $(\mathrm{TMTSF})_2\mathrm{AsF}_6$. In order to investigate the metallic state above 12 K (T_c), where the bolometer is no longer sensitive, we have built a reflectivity chamber and have also used a crystal mosaic. We have, however, taken the *ratio* of the mosaic reflectivity above and below the phase transition at T_c, and have used this together with the low-temperature bolometric reflectance spectrum to obtain the reflectivity above T_c. In this way, we do not have to rely on correcting for the gaps and misalignments of the crystal mosaic by reflecting from it, after it has had gold evaporated onto it, a procedure we so far find to be rather inaccurate.

We find with $(\mathrm{TMTSF})_2\mathrm{AsF}_6$ for the transverse polarization, $\mathbf{E}\|\mathbf{b}'$, that the gap observed previously[17] disappears abruptly on heating through the transition. A sharp *increase* in the interferometer signal of $12\% \pm 1\%$, due to an increase in reflectivity, when concentrating on the limited region from 10 to 50 cm^{-1}, is observed. On the other hand, for the polarization parallel to the stacks, $\mathbf{E}\|\mathbf{a}$, no increase at all is found, and after averaging several runs on different days, we are convinced that we see a decrease of $0.5\% \pm 0.25\%$ over the same spectral range when the temperature is increased from 8 to 15 K. We will show that this must be considered further evidence for a collective mode with a pseudogap along the conducting stacks above the phase transition.

II. EXPERIMENTAL

Crystals of $(\mathrm{TMTSF})\mathrm{AsF}_6$ were grown by one of us (G.S.B.) in a manner already described.[18] A mosaic of 3×6 mm was constructed from 12 crystals, heat sunk with silver paint to two copper bars mounted in a plastic frame with thermal contraction designed to match that of the crystals. This was mounted on the cold finger of an Air Products Heli-tran refrigerator, surrounded by a thick copper radiation shield, all of which was inside a small vacuum shroud with a wedged TPX (Ref. 19) window. The vacuum shroud was attached to the lid of a reflectance module, as shown in Fig. 1, which was placed in a Beckman-RIIC Fourier spectrometer, operated in the polarizing mode with a wire-grid beam splitter and roof-top mirrors. [Earlier attempts[20] to pump the entire reflectance module to high vacuum and avoid the vacuum shroud (C) with the TPX window (D) showed considerable ice condensation on the cold surfaces due to outgassing.] Polarizers and filters at (E) could be changed without disturbing the mosaic. A variable slit (F), just smaller than the mosaic, was focused onto the mosaic, so that only the crystals were illuminated. Beam focus and adjustments could be made by aligning the torroidal mirrors (G) after removing the plexiglass plate (H). With the module evacuated, a visual inspection of the mosaic could always be made through the window. A disadvantage of the slit was the tendency to diffract out of the beam radiation below 10 cm^{-1}. A light cone after the second plane mirror fed the radiation onto a cooled bolometer. Two bolometers were used. The first, with a small thermal conductance, was optimized to work near 30 cm^{-1}, and a cold filter restricted the range to below 60 cm^{-1}. Operating at 2 K, the signal-to-noise ratio in the interferogram was ~ 2000. With 1 cm^{-1} resolution this gave a signal-to-noise ratio in the spectra of ~ 250. Another bolometer, also at 2 K, was used below 300 cm^{-1}. In this region, a Mylar beam splitter was needed, which unfortunately polarizes the beam so that the signal for $\mathbf{E}\|\mathbf{b}'$ was much weaker than for $\mathbf{E}\|\mathbf{a}$. Background spectra were also obtained by rotating the Heli-tran 180° to expose a polished copper disc in the same focal plane as the mosaic. These backgrounds were useful but have not been used in the results to be presented here. During a run, after the mosaic was slowly cooled at 5 K/min to 15 K, the cold tip would be rotated to maximize the signal and then clamped in position. The orientation of the second torroidal mirror would also be optimized and fixed. The temperature would then be cycled between 15 and 7 K with spectra taken at the two temperatures for each polarization. Two diode thermometers, one above and one below the mosaic, were calibrated by measuring the resistance of a crystal of TTF-TCNQ mounted next to the mosaic. 7 K was the lowest temperature obtainable by pumping on the helium in the cold tip. Spectra were also recorded at several temperatures up to 300 K but their usefulness is limited due to the restricted wave-number range.

Results were obtained on the first cooling of the sample, as well as subsequent coolings. No significant effect

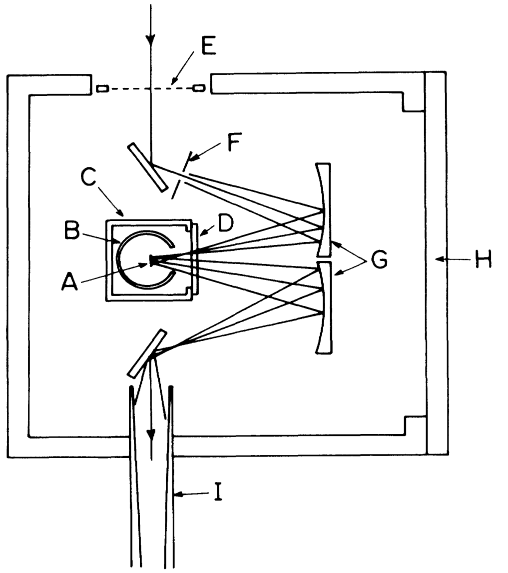

FIG. 1. A horizontal cross section of the reflectance module and sample. A, crystal mosaic and polished copper mirror; B, radiation shield; C, vacuum shroud; D, wedged TPX window; E, polarizers and filters; F, adjustable slit; G, adjustable off-axis torroidal mirrors; H, plexiglass window; I, light cone into bolometer.

of cycling was observed. The vacuum shroud was pumped with a diffusion pump at all times when the sample was cold, and the vacuum maintained between runs. Nevertheless, after five cycles from room temperature the crystal surface appeared slightly pitted, when viewed under a microscope.

An important experimental effect was noticed. When measuring the ratio of $R(15\ \mathrm{K})/R(7\ \mathrm{K})$ for **E**||**b**′, in the 10—50- cm^{-1} range, it was important not to illuminate the sample mosaic with radiation of higher energy. Such radiation had the effect of *reducing* the measured ratio, which we believe to be due to photogenerated carriers masking the gap in the semiconducting phase. No similar effect was observed for **E**||**a**.

III. RESULTS

Figure 2 shows the averaged results obtained for the ratio of the reflected signals at 15 K to those at 7 K for both polarizations. There were no sharp features in the ratio and so a smooth line has been drawn with typical error bars. For **E**||**b**′ the interferometer signal level changes abruptly at 12 K. Figure 2 shows a peak measured ratio of 1.15±0.01 at 15 cm^{-1}, declining to 1.00±0.02 at 300 cm^{-1}. The curve has been extrapolated to 1.18 at zero frequency. Multiplying the 6-K spectrum of Fig. 3 with the ratio of Fig. 2 gives the 15 K reflectivity also seen in Fig. 3. A Kramers-Kronig analysis yields the conductivities shown in Fig. 4. A semiconducting 7 K spectrum with the 70-cm^{-1} peak corresponding to the peak in the combined one-dimensional density of states (see Ref. 17) has changed to a Drude-like metallic conductivity by 15 K. The extrapolated dc conductivity of $\sim 450\ (\Omega\,\mathrm{cm})^{-1}$ is larger than that directly measured for the PF_6 compound[21] $[30\ (\Omega\,\mathrm{cm})^{-1}]$, and the 140 $(\Omega\,\mathrm{cm})^{-1}$ (PF_6) (Ref. 22) and the 80 $(\Omega\,\mathrm{cm})^{-1}$ (AsF_6) (Ref. 11) extrapolated from other infrared measurements. Figure 5 shows a Drude fit to the 15-K **E**||**b**′ conductivity with the plasma frequency $\omega_p = 1580\ \mathrm{cm}^{-1}$ and the damping $\Gamma = 122\ \mathrm{cm}^{-1}$. These should be compared with $\omega_p = 1670\ \mathrm{cm}^{-1}$ and $\Gamma = 350\ \mathrm{cm}^{-1}$ obtained by fitting to the plasma edge.[22] The agreement in ω_p is good. It is possible that the damping is frequency dependent.

Figure 2 shows that for **E**||**a**, the reflectivity *declines* by 0.5%±0.25% between 10 and 300 cm^{-1} at 15 K after the insulator-metal transition. No abrupt changes are seen in the interferometer signal as the temperature is varied. Also shown in Fig. 2 are data indicating a reduction of 1.0%±0.25% by 30 K. R continues to decrease as the temperature is raised (as it also does for **E**||**b**′ above the transition).

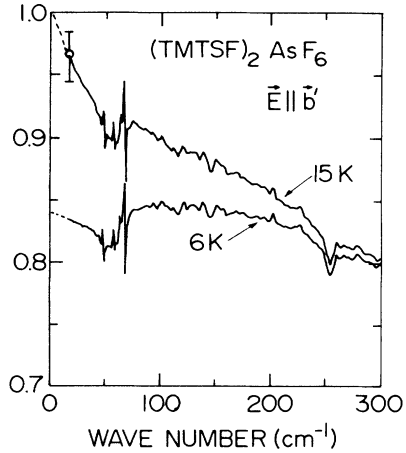

FIG. 3. The **E**||**b**′ reflectivity at 6 K obtained by a composite-bolometer technique, reproduced from Ref. 17, together with the reflectivity at 15 K obtained from the 6-K spectrum and the data in Fig. 2. Dashed lines are extrapolations.

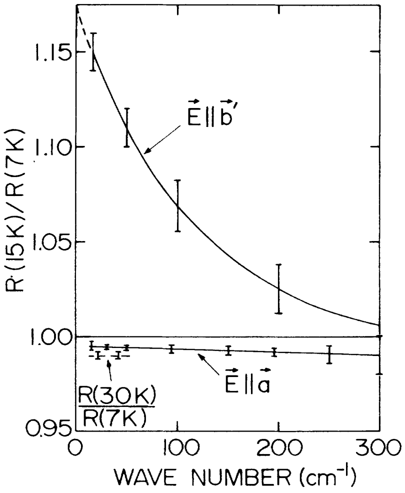

FIG. 2. The measured ratio of reflectance from a crystal mosaic of $(\mathrm{TMTSF})_2\mathrm{AsF}_6$ at 15 K to that at 7 K for two polarizations. The ratio $R(30\ \mathrm{K})/R(7\ \mathrm{K})$ is also given for **E**||**a** between 10 and 50 cm^{-1}.

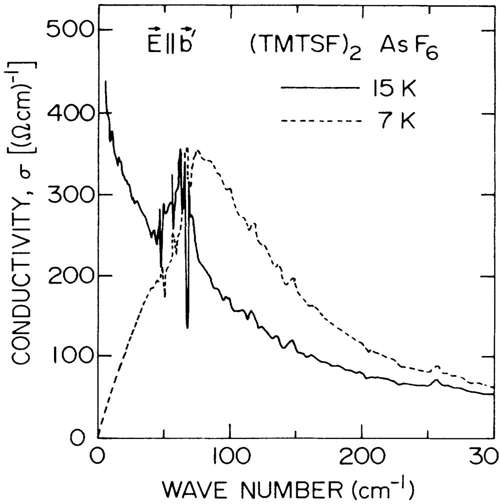

FIG. 4. The conductivity at 15 and 6 K for **E**||**b**′ obtained from Kramers-Kronig analyses of the data in Fig. 3 together with higher-frequency data (see Ref. 17).

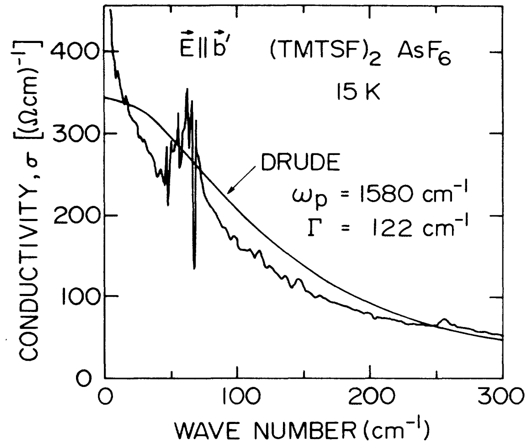

FIG. 5. The $\mathbf{E} \parallel \mathbf{b}'$ conductivity of (TMTSF)$_2$AsF$_6$ at 15 K compared with a Drude form using a plasma frequency, ω_p of 1580 cm^{-1} and a damping Γ of 122 cm^{-1}.

From the ratio in Fig. 2 one obtains the 30-K reflectivity shown in Fig. 6, where it has been assumed that the ratio is constant throughout the spectrum, although only the lower-wave-number portion is important. (The 15-K spectrum lies between the two.) The low-frequency extrapolation is the only linear extrapolation which does not give a negative conductivity below 30 cm^{-1}. The results of the Kramers-Kronig analysis are shown in Fig. 7. The 6-K spectrum reproduced from Ref. 17 shows a gap followed by a peak, again corresponding to the peak in the combined one-dimensional density of states. Below 20 cm^{-1} the conductivity is rising, as it should be if the giant resonance seen in the microwave region by Javadi *et al.*[12] in the PF$_6$ compound is also present here. Above the phase transition at 30 K, the peak has lost strength but the *gap persists,* and the rise below 20 cm^{-1} is now presumably the zero-frequency collective mode. Clearly a great deal is happening between 1 and 10 cm^{-1} in both phases, but no measurements have been made in this difficult region.

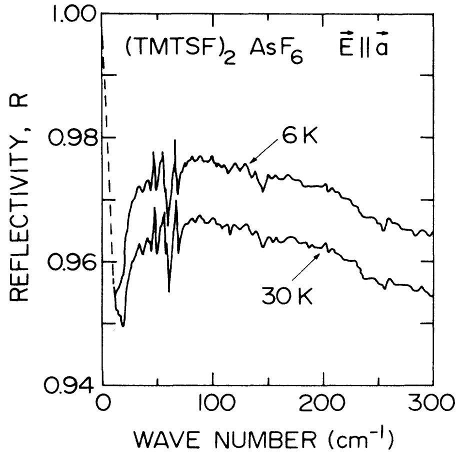

FIG. 6. The $\mathbf{E} \parallel \mathbf{a}$ reflectivity at 6 K obtained by a composite-bolometer technique, reproduced from Ref. 17, together with the reflectivity at 30 K obtained by reducing the 6-K reflectivity by 1%, as indicated in Fig. 2. This assumes the 1% reduction to be valid throughout the entire spectrum. The 15-K spectrum would lie halfway between. The dashed line is a linear extrapolation.

One can attempt to estimate the width of this mode, in two ways. The conductivity sum rule is given by

$$\omega_p^2 = \frac{120}{\pi} \int_0^{\omega_p} \sigma \, d\omega \, , \tag{1}$$

where ω has the units of cm^{-1} and σ is the conductivity in (Ω cm)$^{-1}$. With $\omega_p = 10\,470$ cm^{-1} obtained from a fit[22] to the plasma edge at 30 K, the right-hand side of Eq. (1) gives 9943^2 cm^{-2} at 6 K and 9934^2 cm^{-2} at 15 K, both in good agreement with ω_p^2. If it can be assumed that ω_p has not changed between 6 and 15 K then one can assign the lost oscillator strength to the collective mode. With a dc conductivity[23] of 20 000 (Ω cm)$^{-1}$ at 15 K, one obtains a width of the zero-frequency mode of approximately 6 cm^{-1}.

A second method is described by Jacobsen *et al.*[22] One writes the dielectric constant as a sum of three terms: the high-frequency contribution, the narrow mode at zero frequency, and the strong peak at 70 cm^{-1}. The real part of the dielectric constant is shown in Fig. 8. One sees that it crosses zero at ~6 and ~70 cm^{-1}. If one can describe the 70-cm^{-1} peak as a Lorentzian, and if one can trust the crossing at 6 cm^{-1} (below the range of our data) then a similar analysis to that in Ref. 22 gives a width of the zero-frequency mode of approximately 1 cm^{-1}.

IV. CONCLUSION

We have measured the ratio of the far-infrared reflectivity of a crystal mosaic of (TMTSF)$_2$AsF$_6$ above and below the metal-insulator phase transition at 12 K. Using previously published reflectivity spectra[17] at 6 K, obtained

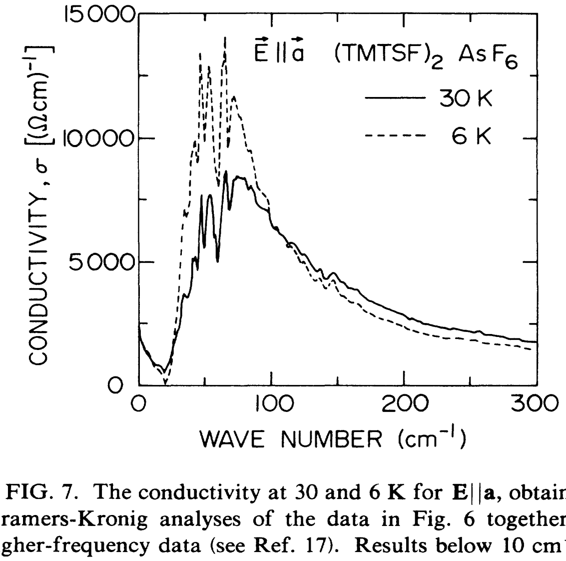

FIG. 7. The conductivity at 30 and 6 K for $\mathbf{E} \parallel \mathbf{a}$, obtained by Kramers-Kronig analyses of the data in Fig. 6 together with higher-frequency data (see Ref. 17). Results below 10 cm^{-1} depend on the chosen extrapolation.

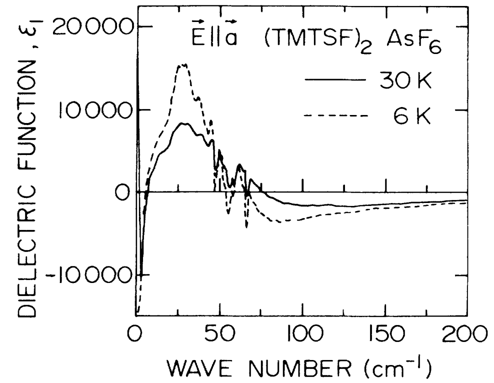

FIG. 8. The real part of the dielectric function, ϵ_1, for **E**||**a** at 30 and 6 K. Zero crossings occur near 6 and 70 cm^{-1}, although everything below 10 cm^{-1} depends on the chosen extrapolation.

by a composite-bolometric technique, we were able to obtain reflectivity spectra at 15 and 30 K. We found an abrupt disappearance of the semiconducting gap at 15 K for radiation polarized perpendicular to the highly conducting axis, **E**||**b**′, replaced by a metallic conductivity. With radiation polarized parallel to the conducting stacks, **E**||**a**, the gap persists up to at least 30 cm^{-1}, while the conductivity peak at 70 cm^{-1} decreases. This is further evidence for a zero-frequency collective mode in the metallic state.

Our results differ from a previous mosaic-reflectivity study of this compound by Ng *et al.*,[11] in a few ways: (a) the size of the effect seen for **E**||**b**′ and the magnitude of the resulting metallic conductivity, and (b) the sign of the reflectivity change for **E**||**a** and the shape of the conductivity above and below the phase transition. As discussed at some length in Ref. 17 we believe these experimental differences to be due to the difficulty of measuring absolute values of R which are close to unity with a mosaic technique. The calculated conductivities also differ due to the completely different approaches. In Ref. 17 we considered the compound at 6 K to be a semiconductor with an energy gap $2\Delta \sim 32$ cm^{-1}, and calculated the conductivity due to vertical electronic transitions across the gap, using the electronic energy bands due to Grant.[24] Peaks were obtained near the maximum of the combined density of electronic states. Good agreement was obtained for **E**||**b** and fair agreement for **E**||**a**. Above the transition, if the gap persists for **E**||**a** then the shape of the conductivity will not greatly change, as we observed. For **E**||**b**, on the other hand, the disappearance of the gap leads to a Drude-type conductivity, with a scattering time determined by surface absorption, impurity scattering, and phonon scattering. In Ref. 11, however, Ng *et al.* considered the compound in its metallic state only, and calculated the **E**||**a** conductivity by considering only phonon scattering (the Holstein volume process). The scattering time due to this process goes to infinity as ω^{-5} for low frequencies and so the calculated conductivity at zero frequency is zero. The broad peak then occurs at the maximum of the phonon density of states, in their case around 200 cm^{-1}.

We reach a similar conclusion, however, regarding the existence of a collective mode in the metallic state. The failure to observe such a mode by Javadi *et al.*[12] in the PF_6 compound would indicate that it is wider than early estimates. Our two estimates from this work for the AsF_6 compound are 1 cm^{-1} and 6 cm^{-1}.

We do not feel that surface effects described by Marianer *et al.*[13] are responsible for the **E**||**a** results since the penetration depth is large at these low frequencies, a high reflectivity was observed in the bolometric experiment, and measurements were taken on the first slow cooling of the sample.

We attempted to compare our results to those obtained by measuring the reflectivity from the mosaic after a layer of gold had been evaporated onto it. Slight damage to one end of the mosaic during handling, however, reduced the overall accuracy to between 10% and 20%, which is too inaccurate to be of use.

ACKNOWLEDGMENT

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[1] D. Jerome, Mol. Cryst. Liq. Cryst. **119**, 1 (1985).

[2] R. L. Green and P. M. Chaikin, in *Proceedings of the 17th International Conference on Low-Temperature Physics, LT17*, edited by U. Eckern, A. Schmidt, W. Weber, and H. Wühl (North-Holland, Amsterdam, 1984).

[3] Marshall J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, Phys. Rev. B **13**, 5111 (1976).

[4] G. A. Thomas *et al.*, Phys. Rev. B **13**, 5105 (1976).

[5] A. Andrieux, H. J. Shulz, D. Jerome, and K. Bechgaard, Phys. Rev. Lett. **43**, 227 (1979).

[6] D. Jerome, in Proceedings of the International Conference on Science and Technology of Synthetic Metals, Kyoto, Japan [Synth. Met. **19**, 259 (1987)].

[7] D. B. Tanner, K. D. Cummings, and C. S. Jacobsen, Phys. Rev. Lett. **47**, 597 (1981).

[8] C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, Mol. Cryst. Liq. Cryst. **79**, 25 (1982).

[9] H. K. Ng, T. Timusk, and K. Bechgaard, J. Phys. (Paris) Colloq. **44**, C3-867 (1983).

[10] H. K. Ng, T. Timusk, and K. Bechgaard, Phys. Rev. B **30**, 5842 (1984).

[11] H. K. Ng, T. Timusk, D. Jerome, and K. Bechgaard, Phys. Rev. B **32**, 8041 (1985).

[12] H. H. S. Javadi, S. Sridhar, G. Gruner, L. Chiang, and F. Wudl, Phys. Rev. Lett. **55**, 1216 (1985).

[13] S. Marianer, M. Kaveh, and M. Weger, Phys. Rev. B **25**, 5197 (1982).

[14] Frances E. Bates, J. E. Eldridge, and M. R. Bryce, Can. J.

Phys. **59**, 339 (1981).

[15] J. E. Eldridge, Phys. Rev. B **31**, 5465 (1985); J. E. Eldridge and Frances E. Bates, *ibid.* **28**, 6972 (1983).

[16] J. E. Eldridge and G. S. Bates. Mol. Cryst. Liq. Cryst. **119**, 183 (1985).

[17] J. E. Eldridge and G. S. Bates. Phys. Rev. B **34**, 6992 (1986).

[18] J. E. Eldridge, C. C. Homes, Frances E. Bates, and G. S. Bates, Phys. Rev. B **32**, 5156 (1985).

[19] TPX is the Mitsui and Co., Ltd. trademark for methylpentene polymer.

[20] K. E. Kornelsen, M. Sc. thesis, University of British Columbia, 1986.

[21] C. S. Jacobsen, K. Mortensen, M. Weger, and K. Bechgaard, Solid State Commun. **38**, 423 (1981).

[22] C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, Phys. Rev. B **28**, 7019 (1983).

[23] J. B. Torrance, J. Phys. (Paris) Colloq. **44**, C3-799 (1983).

[24] P. M. Grant, Phys. Rev. Lett. **13**, 1005 (1983).