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Dimensionality Crossover in the Organic Superconductor Tetramethyltetraselenafulvalene Hexafluorophosphate [(TMTSF)$_2$PF$_6$]

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Polarized reflectance measurements from the far infrared to the visible are reported for (TMTSF)$_2$PF$_6$. At low temperatures, both parallel and perpendicular polarizations show plasma edges in the infrared with metallic reflection below these edges, indicating two- or three-dimensional behavior. The transverse plasma frequency is $\sim \frac{1}{5}$ of the parallel plasma frequency. At higher temperatures, the plasmon in the perpendicular polarization becomes highly overdamped, indicating a crossover to one-dimensional behavior.

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The organic linear-chain compound bis-tetramethyltetraselenafulvalene hexafluorophosphate, (TMTSF)$_2$PF$_6$, is currently of great interest because it remains metallic to low temperatures[1] (19 K) and because it becomes superconducting[2] (when subjected to a hydrostatic pressure of 12 kbar and cooled below 0.9 K). It is the first-known organic superconductor. These properties are somewhat surprising in view of its structure,[3] highly anisotropic dc conductivity, and near-infrared reflectance,[1] which suggest that (TMTSF)$_2$PF$_6$ is at least as one-dimensional (1D) as tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ).[4] It is generally believed, as demonstrated experimentally in the case of TTF-TCNQ, that because of the Peierls transition, quasi-1D systems should exhibit neither superconductivity nor low-temperature metallic behavior.[5]

A recent interpretation based on the pressure dependence of the transition temperatures in (TMTSF)$_2$PF$_6$ suggests that the material may be electronically 2D or 3D at low temperature.[6] In this Letter we present direct evidence for considerable overlap transverse to the chain direction. With decreasing temperature we have observed the growth of an infrared reflectance edge for electric field perpendicular to the chain direction, which strongly resembles the plasma edge of a Drude metal. Such an edge has not been previously observed in organic linear-chain conductors; we suggest that it results from a significant transverse bandwidth. At high temperature the edge is overdamped. Thus from the optical point of view (TMTSF)$_2$PF$_6$ must be considered a 1D metal at high temperature, while it is 2D or 3D at low temperature. The crossover from one regime to the other occurs when $kT \sim W_\perp$, where $W_\perp$ is the transverse bandwidth. At higher temperatures thermal disorder localizes electrons on single chains (leading to diffusive trans-

port), while at lower temperatures it is possible to have coherent motion in the transverse direction.

The crystal structure of $(TMTSF)_2PF_6$ is triclinic with sheets of 1D TMTSF stacks separated by sheets of PF_6^- ions.[3] The stacking axis is a and the sheets are in the $a-b$ plane. There is a zig-zag arrangement of the TMTSF molecules of an individual stack and a small (1.14°) tilt of the molecules away from the perpendicular. This tilt causes a weak dimerization of the molecules leading in an extended zone scheme to a 1D band structure consisting of one cosinelike band with a very small gap in the center. Because the PF_6^- ion has a very stable, closed-shell electronic structure, each TMTSF molecule can be assumed to have a charge of $+\frac{1}{2}$, leading to $k_F = 3\pi/2a$, where a is the chain-axis lattice constant comprising two molecules. If there is a sufficiently large transverse overlap integral, there will be a significant transverse bandwidth. From the crystal structure and the resistivity anisotropy[7] the biggest transverse overlap is expected to be in the TMTSF sheets, i.e., in the b direction.

Single crystals of $(TMTSF)_2PF_6$ were prepared as described elsewhere.[1] Microanalysis showed 2:1 stoichiometry within experimental limits (0.5%). All of the crystals were elongated in the a direction and had reasonable quality (001) faces. The reflectance studies were made for electric fields along the chain axis, a, and perpendicular to a in the plane parallel to the TMTSF sheets, the b' direction.

The reflectance data were taken by using two instruments. The frequency range 600–20 000 cm^{-1} (0.08–2.5 eV) was covered by a Perkin-Elmer model-16U grating monochromator. Sufficient signal was obtained from single crystals with faces of approximate size 5×0.7 mm^2. The far-infrared measurements covering the range 10–700 cm^{-1} (1.25 meV to 0.09 eV) were done on a Michelson interferometer. Here a mosaic of eight crystals, optically aligned to give a target of 6×6 mm^2, was needed to give sufficient signal. Absolute values of reflectance were obtained in both cases by comparing the signal from the naked crystal surfaces to the signal from gold-covered crystal surfaces.

Low-temperature measurements were performed in a Helitran cryostat with electronic temperature control. Because of radiation heating, the sample was warmer than the indicated temperature of the cryostat. The true sample temperatures were determined by placing a TTF-

TCNQ crystal in the sample position and by using the well-known resistivity versus temperature of this material[8] as a calibration. When the cold-finger thermometer indicated 4.2 K, the actual crystal temperature was 25 K; at 100 K and above, the difference was negligible.

In Figs. 1(a)–1(c) we present the reflectance data for $(TMTSF)_2PF_6$ for light polarized parallel
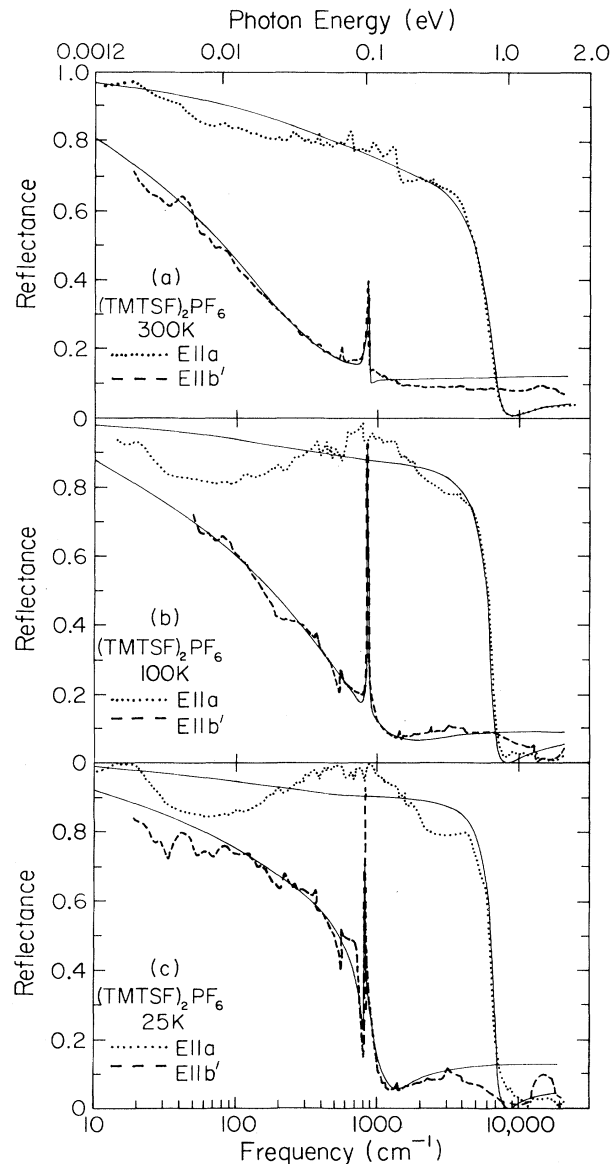

FIG. 1. Polarized reflectance of $(TMTSF)_2PF_6$ for $\vec{E} \parallel \vec{a}$ (conducting axis) and $\vec{E} \parallel \vec{b}'$ (perpendicular to $\vec{a}$ in the sheets of TMTSF molecules or PF_6^- ions). Data are shown for three temperatures: (a) 300 K, (b) 100 K, and (c) 25 K. Least-squares fits to the reflectance, assuming a Drude dielectric function, Eq. (1), are shown as solid lines.

to the a and b' directions at three temperatures: 300, 100, and 25 K. There are a wealth of complicated details in the reflectance spectra; the following features seem most noteworthy:

The chain-axis reflectance ($\vec{E} \parallel \vec{a}$) appears metallic at 300 K, as expected, with a plasma edge near 7000 cm^{-1}. At lower frequencies, the reflectance gradually rises toward unity. In the infrared range, strong vibronic structure is seen. The sharp rise below 1300 cm^{-1} resembles a similar feature observed[9] in TTF-TCNQ and is believed to be due to coupling of C=C molecular vibrations to the conduction electrons. The position of the plasma edge is temperature independent to first approximation but the edge sharpens considerably on cooling to 100 K, Fig. 1(b), and then to 25 K, Fig. 1(c). At these temperatures a broad maximum extending from 300 to 1000 cm^{-1} approaches reflectance values of 100% as does the very-low-frequency reflectance. The minimum at 50 cm^{-1} may be due to a Fano-type interference[10] of the electronic background with lattice vibrational modes.

The reflectivity for $\vec{E} \parallel \vec{b}'$ at 300 K is rather flat down to 1200 cm^{-1}. At lower frequencies, $R(b')$ increases from the 10% level to about 70% at the lowest frequencies measured. This behavior is characteristic of a conducting material where the optical relaxation rate is much higher than the plasma frequency, i.e., the plasmons are overdamped.

Perhaps the most interesting feature of the data is that, as the temperature is lowered, a rather well-defined reflectance edge, along with an associated minimum near 1000 cm^{-1}, appears. We interpret this edge as the true transverse plasma edge. Thus at low temperatures well-defined plasmons apparently exist in at least two dimensions. To our knowledge this is the first observation of a strongly anisotropic, but not quasi-1D plasmon behavior in the class of organic charge-transfer salts. For comparison, the corresponding reflectance component in the isomorphous sulfur analog to (TMTSF)$_2$PF$_6$ is flat down to at least 500 cm^{-1} at high as well as at low temperature.

It is important to stress that the transverse reflectance data cannot be explained as an optical-phonon excitation. The electric field direction for exciting an ionic-type vibration would be along the c axis, not the b' axis. In addition, as shall be discussed below, the oscillator strength implied by these data is more than 2 orders of magnitude larger than appropriate for a lattice optical phonon.

Another detail of the $\vec{E} \parallel \vec{b}'$ data is the very strong infrared absorption band of the PF$_6^-$ ion[11] at 835 cm^{-1}. This band is known to have a high oscillator strength. The other infrared band of PF$_6^-$ at 558 cm^{-1} is also seen in the data, again most clearly for $\vec{E} \parallel \vec{b}'$. Such vibrational modes, not coupled to the conduction electrons, are difficult to identify in the highly reflecting a-axis spectra.

The optical properties of quasi-1D conductors are customarily analyzed in terms of simple Drude models, for which the dielectric function $\epsilon(\omega)$ obeys

$$\epsilon(\omega) = \epsilon_{\text{core}} - \omega_p^2 / \omega(\omega + i\Gamma), \tag{1}$$

where ϵ_{core} is the background dielectric constant, ω_p the unscreened plasma frequency, and Γ the optical relaxation rate. In Table I we give the values of ω_p, Γ, and ϵ_{core} obtained by fitting the reflectance for the two polarizations and the three temperatures, assuming a Drude dielectric function, Eq. (1). The fits are shown as solid lines in Fig. 1.

The results of these fits allow us to obtain band-structure parameters for (TMTSF)$_2$PF$_6$. The optical effective mass, m^*, is related to the plasma frequency by the equation

$$\omega_p^2 = 4\pi n e^2 / m^*. \tag{2}$$

TABLE I. Drude-model parameters for (TMTSF)$_2$PF$_6$. Note that the fit to data for $\vec{E} \parallel \vec{b}'$ included a narrow Lorentzian oscillator to account for the observed line at 835 cm^{-1}.

T (K)	$\omega_{p'a}$ (cm^{-1})	Γ_a (cm^{-1})	$\epsilon_{\text{core}, a}$	$\omega_{p,b'}$ (cm^{-1})	$\Gamma_{b'}$ (cm^{-1})	$\epsilon_{\text{core}, b'}$
300	11 200	1920	2.6	2340	3670	4.3
100	11 300	780	2.9	2360	1700	3.6
25	11 400	580	2.9	2360	600	4.5

At all temperatures we find $m^*(a)/m_e \simeq 1.0$ and $m^*(b')/m_e \simeq 20$. It is remarkable that the chain-axis effective mass is close to the free-electron mass. In TTF-TCNQ, for comparison,[9] $m^* \simeq 3m_e$. Using a simple tight-binding model for the band structure, we can translate these effective-mass values into bandwidths:

$$W = 2\hbar^2/m^*l^2, \tag{3}$$

where l is the intermolecular spacing. For simplicity the optical effective mass has been taken as the band-edge effective mass. From (3) we obtain $W(a) \simeq 1.2$ eV and $W(b') \simeq 13$ meV.

For an effective mass nearly equal to the free-electron value, the tight-binding model is clearly not the best one and a more realistic band-structure calculation on $(TMTSF)_2PF_6$ would be quite important. However, the estimates given here underscore two interesting facts: The bandwidth of the TMTSF stacks is unusually high for charge-transfer complexes, where bandwidth estimates tend to be around 0.5 eV. A chain-axis bandwidth of about 1 eV is also supported by an independent estimate from thermopower data.[1] Bandwidths in excess of 1 eV have previously been found only in systems with very efficient overlap of donor molecules, such as (tetrathiatetracene)$_2$(iodide)$_3$ (TTT_2I_3)[12] and tetrathiafulvalenium iodide $(TTFI_{0.7})$.[13]

A transverse band mass of $20m_e$ seems rather high. It is an open question whether the Drude analysis yields the correct value in the high-mass limit. However, we believe that it is reasonable as a first approximation, since the bandwidth anisotropy found here is independently confirmed by the resistivity anisotropy. The simple relation[14]

$$\frac{\rho(a)}{\rho(b')} = \left(\frac{W(b')}{W(a)}\right)^2 \frac{2b}{a} \tag{4}$$

yields a predicted anisotropy $\rho(a)/\rho(b') = 1.7 \times 10^{-4}$. The experimental anisotropy at low temperature[7] is 3×10^{-4} in good agreement with this number.

The data indicate a dimensionality crossover in two ways. (1) The infrared reflectance goes from 1D to at least 2D (although anisotropic) metallic behavior, as the temperature is lowered. Whether this observation in itself has relation to superconductivity and suppression of the Peierls transition is not clear. (2) If the derived transverse bandwidth, $W(b') = 13$ meV, is assumed to be correct, the smearing of the Fermi-Dirac function is smaller than $W(b')$ only at low temperatures. Thus at room temperature the band structure is effectively 1D, while below 100 K, $W(b')$ will become increasingly important. Here may be implications for superconductivity in this material. In 1D materials, the Peierls transition generally defeats any tendency towards superconducting behavior. In $(TMTSF)_2PF_6$, the transverse coupling gives considerable Fermi surface curvature and suppresses the Peierls transition (particularly at high pressures[2]) to a sufficient extent that the superconducting transition can occur.

In summary $(TMTSF)_2PF_6$ has been found to possess highly anisotropic optical properties. But, in contrast to other quasi-1D materials, metallic behavior is also seen perpendicular to the chain axis at low temperatures.

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