Magnetic Quantum Oscillations in Tetramethyltetraselenafulvalenium Hexafluorophosphate [$(TMTSF)_2PF_6$]

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The metallic (high-pressure) phase of $(TMTSF)_2PF_6$ exhibits Shubnikov–de Haas resistance variations at low temperatures. A single frequency of 0.76 MG has been recorded. A large anisotropy in the transverse magnetoresistance is also observed. Our results imply a two-dimensional Fermi surface under pressure, with compensated electron and hole sections oriented along the crystal c axis. Some unusual and physically significant anomalies associated with the oscillations are discussed.

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The recently synthesized organic conductor $(TMTSF)_2PF_6$ (*bis*-tetramethyltetraselenafulvalenium hexafluorophosphate, hereafter called TSP)[1] has exhibited a variety of fascinating and distinctive properties, including very high conductivity ($> 10^5$ S/cm), a low metal-insulator transition temperature, superconductivity under modest pressure ($T_c = 1.2$ K at 6.5 kbar),[2-4] nonlinear electric field effects,[5-6] and a spin-density-wave (SDW) ground state at ambient pressure.[5,7] Many of these properties result from the quasi-one-dimensional structure of TSP. However, as has been shown in the studies of other one-dimensional (1D) conductors, the degree and nature of the electronic coupling between chains is very important for understanding the properties of these materials.[8] In the case of TSP, two views have emerged as to the dimensionality of the low-temperature, high-pressure ($P > 6.5$ kbar) state. Jerome *et al.*[2] believe that in this state TSP is highly 1D with a wide temperature region (up to 20 K) of 1D fluctuation effects, while Greene and Engler[4] have presented transport data suggesting that TSP is an anisotropic 2D or 3D metal.

In this Letter we report the first observation of Shubnikov–de Haas (SdH) oscillations in the resistivity of TSP. The mere fact of this observation is definitive evidence that the low-temperature, high-pressure state of TSP is *multidimensional* in nature. In fact, detailed analysis of our data implies a 2D Fermi surface. The oscillations exhibited by TSP do, however, show some unusual behavior which may be related to the continued occurrence of SDW's at high pressures in the metallic state.

The crystals used in the present study were electrochemically grown[1,4] and had typical dimensions $0.4\times 0.015\times 0.005$ cm^3. Resistance was measured with a linear four-probe arrangement of gold-paste contacts along the highly conducting crystal a axis. dc excitation currents were used for data involving field modulation, and ac otherwise. Pressure was applied to the system by means of a helium pressurization system,[9] with an absolute accuracy of 0.2 kbar and resolution of 0.1 kbar. The use of helium pressure is particularly advantageous for working with TSP. Since the pressures generated are much more nearly hydrostatic than with liquid-medium systems, the brittle samples are subjected to much lower stresses. Furthermore, the pressure applied to the samples can be changed while maintaining the sample temperature below 60 K.

Magnetic fields were applied with a high-uniformity 100-kOe magnet designed for de Haas–van Alphen studies. The magnet is freely rotatable in the plane transverse to the sample a axis, along which the current flowed. Note that all references in this Letter to crystal directions are meant to be approximate (usually $\pm 10°$) and hence are not affected by the triclinic character of the crystals.

Data on the oscillations were obtained by modulating the field using independent coils, typically with 500 G amplitude at 50 Hz. With dc current applied to the sample, the voltage response at this frequency or its harmonics could be obtained with a lock-in amplifier. Third-harmonic (150 Hz) detection proved the best compromise for eliminating the undesired semiclassical magnetoresistive background while preserving sufficient amplitude to observe the desired oscillations.

Great care was taken in the pressurization and cooling of the crystals to minimize stress-induced cracking, with variable success. Our best (least damaged) samples showed low-temperature conductivities $>10^5$ S/cm and reproduced the known T_c vs P phase diagram[3,4]; these were usually the crystals in which oscillations were detected. Quantitative resistance measurements have been difficult to obtain, because of inhomogeneous, relatively resistive contacts.[10] This did not, however, affect our ability to make quantitative measurements on the oscillations.

Figure 1 shows nominal resistance data for one crystal at 1.1 K under 7.4 kbar pressure versus magnetic field for two sample orientations. These data, while not quantitative, serve to illustrate salient features present in all the samples investigated: The transverse magnetoresistance is highly anisotropic for H in the b-c crystal plane —tending to saturation for $H \perp c$, and rising steeply with field for $H \parallel c$, where the oscillations appear. Jacobsen *et al.*[11] have reported magnetoresistance measurements at higher temperatures and at ambient pressure. Their observation of a small (<2) anisotropy for magnetic fields in the b-c crystal plane differs sharply from the present results. This suggests that pressure enhances the b-axis coupling, eventually resulting in closed orbits in the a-b plane as evidenced by the occurrence of oscillations for $H \parallel c$. Moreover, the combination for $H \parallel c$ of closed orbits and nonsaturating magnetoresistance implies that TSP is a compensated metal (there are equivalent electron and hole sections). Thus the resistance saturation for $H \perp c$ ($H \parallel b$) implies an open orbit extending along the c axis [theory predicts $\rho \sim H^2 \cos^2\alpha$ for a compensated metal, where α is the angle between the current and the open direction].[12] This is consistent with the lack of oscillations for $H \parallel b$, with the crystal structure,[13] and with the anisotropy in the conductivity,[11] provided the Fermi surface sections are envisioned as flattened in the a direction. It is clear then that the Fermi surface of TSP under pressure cannot be described as quasi one dimensional, but is essentially two dimensional in nature.

Oscillations have been observed in four samples thus far; that is, in all the samples pressurized and cooled without extensive damage. Raw data for one of these samples of the third harmonic signal plotted versus field are presented in Fig. 2. These data were taken at 1.1 K under 6.9 kbar pressure, with $H \parallel c$. It will be convenient in discussing the data to write down descriptive equations. Following essentially the treatment of Roth and Argyres,[14] the resistive oscillations are given by

$$\frac{\Delta\rho}{\rho_{sc}} = \sum_i \sum_{r=1}^{\infty} b_{ir} \cos(2\pi r F_i/H - \Phi_{ir}), \tag{1}$$

where ρ_{sc} is the semiclassical magnetoresistance,

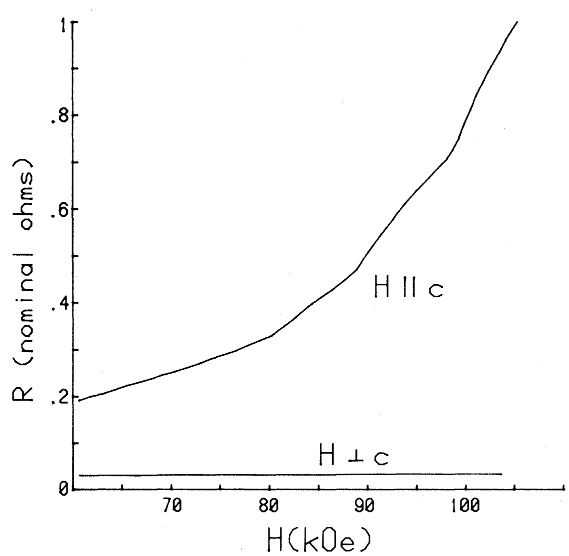

FIG. 1. Nominal resistive a-axis signal from a single crystal vs magnetic field at $T = 1.1$ K and $P = 7.4$ kbar for fields oriented roughly parallel and perpendicular to the crystal c axis.

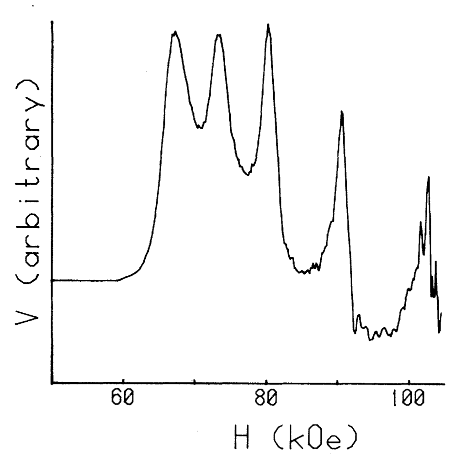

FIG. 2. Signal at 150 Hz with constant-amplitude 50-Hz field modulation vs magnetic field (raw data). $T = 1.1$ K, $P = 6.9$ kbar.

and

$$b_{ir} = \frac{1}{\sqrt{r}}\left(\frac{H}{2F_i}\right)^{1/2} \frac{X_{ir}}{\sinh X_{ir}} \frac{\cos(\pi \nu_{ir})}{\exp(2\pi^2 r k X_D/\mu_i H)}. \quad (2)$$

$F_i = cA_i/eh$ is the de Haas–van Alphen (dHvA) frequency of the ith orbit of extremal area A_i; r denotes harmonics of this frequency; Φ_{ir} is a phase factor; $\mu_i = eh/m_i^* c$, with $m_i^* \equiv (1/2\pi)(\delta A_i/\delta\epsilon)_{\epsilon_F}$ the effective mass; $\nu_{ir} = r(gm_i^*/2m)$ with g the spin factor; $X_{ir} = 2\pi^2 rkT/\mu_i H$; and X_D is the Dingle temperature, which accounts for level broadening due to scattering.

Figure 3, in which are plotted successive integers incrementally assigned to each peak versus inverse field at the corresponding peak, shows the periodicity expected from Eq. (1) for a single orbit with frequency 0.76 ± 0.03 MG. This frequency increases with angle (as the field deviates from the c axis) approximately as expected for a cylindrical Fermi surface oriented along the c direction: $F(\theta) = F(0)/\cos\theta$. Data were obtained only for $\theta < 20°$ because of loss of amplitude at higher angles. Furthermore, the signal amplitude falls with rising temperature as expected; a simple analysis based on Eqs. (1) and (2), but neglecting the semiclassical background and using only the first dHvA harmonic [$r = 1$ in Eq. (1)], yields a good fit with $m^* \cong 1.1$. A similar derivation from the field dependence of the signal amplitude yields $X_D \sim 3$ K (sample dependent).[15]

So it is seen that these data show the behavior expected from Shubnikov–de Haas oscillations.

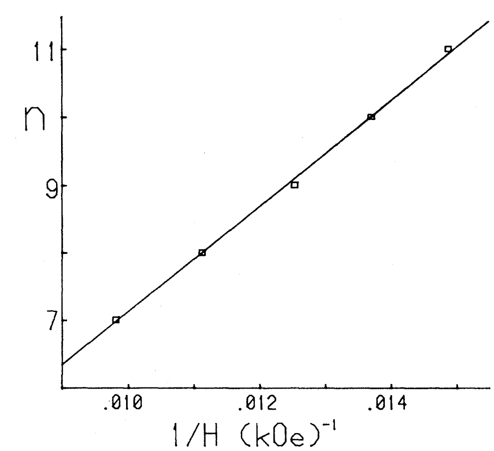

FIG. 3. Successive integers for the peaks in Fig. 2 vs inverse magnetic field (see text). The Shubnikov–de Haas frequency is given by $dn/d(1/H)$.

There are several unusual anomalies however. The oscillations have a low frequency corresponding to only 1% of a Brillouin zone cross section,[12] yet apparently have a large effective mass. This discrepancy would be difficult to account for even in bands containing dominant d or f character, and does not seem consistent with the bonding expected in TSP. Moreover, with the large mass and Dingle temperature, one would not expect higher harmonic terms to contribute significantly to the peak shapes. This is definitely not the case, as Fig. 2 shows.

The problem may lie in the analyses used to derive m^* and X_D, but correcting these does not seem likely to overcome the magnitude of the discrepancy. There is an attractive possible explanation based upon the proposed occurrence of SDW's in TSP.[5,8] Schlottman and Falicov[16] have pointed out that an order parameter associated with such a collective effect would alter the electronic free energy in a magnetic field, resulting in interference between oscillations from the various Fermi surface sections. In particular, a beat frequency would appear which could be much lower than either original frequency but whose mass is the sum of the original masses. In the case of TSP with $m^* \sim 1$, if the parent oscillations each had $m^* \sim 0.5$ their amplitude would be damped by the cosine term in Eq. (2) (assuming $g \sim 2$),[17] consistent with the failure to observe such frequencies. It is not necessary to have damping for the model to be applicable, however, since high-frequency SdH oscillations are usually more difficult to see anyway than those at low frequencies [consistent with Eq. (2)]. Note that this interference mechanism requires the presence of SDW's (or similar collective phenomenon) in the *high*-pressure state of TSP; this suggests the possible coexistence of SDW's and superconductivity in TSP.

Again referring to Fig. 2, we see that the oscillations vanish abruptly below ~65 kOe at 6.9 kbar for $H \parallel c$. This "turn-on" position (H_{t0}) of the lowest peak goes up by more than 10 kOe at 8 kbar. The angular variation of H_{t0} follows the inverse of the cosine of the angle between H and the c axis. The usual explanation for such a threshold involves magnetic breakdown of the Fermi surface, but this should be a much more gradual effect than what is observed. We do not at this time have a viable explanation for this effect.

In summary, we have observed Shubnikov–de Haas oscillations in $(TMTSF)_2PF_6$. Only one frequency, 0.76 MG, has been identified. The apparent effective mass and Dingle temperature values are 1.1 and 3 K, respectively. The oscillations appear only for H approximately parallel to the c axis, requiring the presence of closed orbits in the a-b plane. Their frequency varies as $(\cos\theta)^{-1}$, implying that the orbits are open along the c axis, consistent with the magnetoresistance. Therefore the Fermi surface appears to be essentially two dimensional. The data also imply that the material is a compensated metal, with both electron and hole surfaces. Anomalies have been found associated with the effect, which may be related to many-body correlations and to magnetic breakdown.

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Multisoliton Excitations in Long Josephson Junctions

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The microwave emission from long Josephson tunnel junctions dc-current biased on zero-field and Fiske steps has been measured. The frequency and power variation on all steps of the narrow-linewidth radiation near the fundamental cavity-mode frequency and the observed transitions between different modes on a given step may be understood in a picture of multifluxon excitations with propagation of different bunched fluxon configurations depending on the current and magnetic field bias.

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The concept of soliton excitations of Josephson tunnel junctions was introduced in order to explain the so-called zero-field steps (ZFS) in the current-voltage characteristic of long tunnel junctions.[1] The soliton or fluxon is a $\pm 2\pi$ kink in the phase difference across the barrier encom-

