Pressure Dependence of Superconductivity in an Organic Superconductor *bis*-Tetramethyltetraselenafulvalene Hexafluorophosphate

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The transition temperature of *bis*-tetramethyltetraselenafulvalene hexafluorophosphate $(TMTSF)_2PF_6$ is found to decrease for pressures up to 12 kbar at a rate $dT_c/dP = (-8 \pm 1)\times 10^{-5}$ K/bar. At 6.5 kbar, a coexistence of superconductivity ($T_c \sim 1.1$ K) and a metal-insulator transition ($T_{MI} \sim 6$ K) is found.

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Recently, Jerome *et al.*[1] reported the first observation of superconductivity in an organic solid, *bis*-tetramethyltetraselenafulvalene hexafluorophosphate $[(TMTSF)_2PF_6]$, with a transition temperature $T_c \sim 0.9$ K at 12 kbar of applied pressure. Moreover, they suggested that significant superconducting fluctuations might exist at temperatures as high as 20 K. At ambient pressure this anisotropic organic conductor has a number of other interesting properties: a metal-insulator transition temperature that is rather low[2] ($T_{MI} \sim 19$ K), electrical conductivity (σ) exceeding 10^5 Ω^{-1} cm^{-1} near T_{MI}, nonlinear σ at small electric fields[3] below T_{MI}, and an unusual magnetic susceptibility[4] below T_{MI}. The exact origin of T_{MI} is not known, but may be due to the formation of a spin-density-wave ground state.[3,4]

In this paper we report the first measurements of the pressure (P) dependence of the superconductivity in $(TMTSF)_2PF_6$. Besides confirming the existence of superconductivity, our data provide two new interesting results: (1) At $P \sim 6.5$ kbar both superconductivity and a metal-insulator transition appear to coexist, and (2) T_c decreases sharply with increasing pressure. We believe these results are significant for several reasons. First, this material is the only one (to our knowledge) to exhibit superconductivity in the presence of an apparent gap over most of the Fermi surface (as suggested by a strongly increasing resistance between T_{MI} and T_c). Secondly, our results argue against the view that important superconducting fluctuation effects occur for $T > T_c$. The former result will be important as a comparison with theories[5,6] that predict the conditions under which spin-density waves (SDW) or charge-density waves (CDW) and superconductivity (SC) can exist in low-dimensional metals.

The single crystals used in the present study were obtained by an electrochemical technique similar to that described by Bechgaard[2] but with constant-voltage conditions. The resistivity (ρ) was measured by a four-probe ac ($\nu \sim 100$ Hz) technique, with gold-paste contacts. Pressure measurements were made using a beryllium-copper-clamped device with *n*-heptane as the pressure medium. The pressure was measured at low temperature with a lead manometer.

In Fig. 1, we show the four-probe resistance of a typical $(TMTSF)_2PF_6$ crystal for $T < 4.2$ K at 6.5 and 10.5 kbar and transverse magnetic field ($H_\perp$ nearly parallel to *b* axis) equal to 0 and 41 kOe. At 6.5 kbar, we have both an activated region and a superconducting transition ($T_c \sim 1.1$ K)

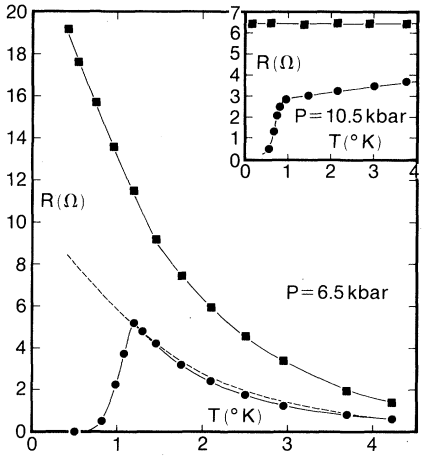

FIG. 1. Resistance of a crystal of $(TMTSF)_2PF_6$ along the *a* axis below 4.2 K at pressure 6.5 and 10.5 kbar (inset). Transverse (nearly parallel to *b* axis) magnetic field $H_\perp = 0$ (solid circles) and 41 kOe (solid squares). Dashed line is discussed in text.

coexisting. Increasing $H_\perp$ leads to a decrease in T_c (with $H_{c\perp} \sim 3$ kOe) and a continuation of the activated $\rho(T)$ down to 50 mK (our limit). The minimum in the normal state ρ_a occurs at $T_{min} \sim 6$ K above which $\rho \propto T$ up to ~55 K. At 10.5 kbar on the same sample, the temperature dependence of ρ has changed dramatically, and we find $T_c \sim 0.8$ K with $\rho \propto T$ from T_c to 60 K. At ambient pressure our samples have T_{MI} [as defined by $(1/R)dR/dT|_{max}$] at 12.5 K. Other workers[1,2] report T_{MI} ~15–19 K. This difference may account for why we observe superconductivity at a higher T_c and lower applied pressure than Jerome *et al.*[1]

Our results at 6.5 kbar are unusual. They suggest that superconductivity exists even in the presence of a gap over most of the Fermi surface. Surprisingly when the gap is removed at 10 kbar, the extra electron density of states, $N(\epsilon_F)$, does not help increase T_c. Actually, at 6.5 kbar we find that, below $T \sim 2.5$ K, $\rho_a(T)$ increases much slower than a true activation behavior [(i.e., $\rho = \rho_0 \times \exp(\Delta/kT)$]. We have found the same behavior for $\rho_a(T)$ at ambient pressure below $T \sim 2.5$ K. It seems likely from the thermopower studies[2] that impurity states are present in the gap and these can dominate the low-T resistivity. At 6.5 kbar we also observe strong nonlinear electric field (for $E > 50$ mV/cm) effects for $T \leq T_{min}$. These will be reported in detail elsewhere, but they are similar to what has been found at ambient pressure.[7] This suggests that the physical origin of T_{MI} is the same at 6.5 kbar and ambient pressure. At 10 kbar when T_{MI} is gone, the E field effects are absent at all T (for E up to our limit of 4 V/cm).

We believe the most likely explanation for our results is that under pressure $(TMTSF)_2PF_6$ has become a more two-dimensional (2D) or three-dimensional system. In 2D materials, the coexistence of SC and CDW's is well known, although in these systems (in contrast to results here) there is always a metallic $\rho(T)$ above T_c (i.e., the Fermi surface has regions without gaps). We have measured a strong decrease in the electrical anisotropy under pressure. For example, at 300 K, σ_b increases a factor of ~7 by 10 kbar (note that b is approximately the direction of maximum Se-Se interaction), whereas σ_a changes only slightly. Thus we estimate $\sigma_a(300\text{ K})/\sigma_b(300\text{ K})$ to be ~7 at 10 kbar, whereas it is ≃50 at ambient P in our samples. At 10 kbar we find $\rho_b(300\text{ K})/\rho_b(4.2\text{ K}) \simeq \rho_a(300\text{ K})/\rho_a(4.2\text{ K})$, which implies $\sigma_a(4.2\text{ K})/\sigma_b(4.2\text{ K}) \simeq 7$. Since near T_{MI} at ambient pressure $\sigma_a(20\text{ K})/\sigma_b(20\text{ K})$ is reported[8] to be greater than 1000, our results show that the low-temperature anisotropy is greatly reduced under pressure. This trend towards higher dimensionality would explain naturally the decrease in T_{MI} with pressure (if we assume a Peierls-type transition) and the coexistence of superconductivity and SDW. To verify these ideas quantitatively, it will be necessary to make more detailed measurements in the pressure range below 6.5 kbar and between 6.5 and 10.5 kbar.

Another explanation for our data at 6.5 kbar is that the superconductivity is filamentary and caused by nonhydrostatic pressure effects. To check this we have measured the critical current (J_c) by a pulse technique (to avoid heating) on the same sample (at $T/T_c \sim 0.4$) for the three pressures shown in Fig. 2. We find at all pressures a similar J_c, $J_c \sim 0.1$ A/mm^2 for one sample, and $J_c \sim 0.2$ A/mm^2 for another. Thus, if the superconductivity would be filamentary at 6.5 kbar, it must also be filamentary at higher pressure. On the other hand, we observe a higher $H_{c\perp}$ at 6.5 kbar than at 10 kbar (3000 vs 600 Oe) as well as some anomalous curvature near T_c. This might imply a SC state of weak coupling or even a filament; however, it has been suggested[9] that the anomalous curvature could result from a situation where SC and CDW's coexist, in agreement with our previous ideas. Thus, although we believe our evidence is good for the coexistence of SC and a T_{MI}, more work will be necessary to completely rule out the filament possibility.

The pressure dependence of T_c for this sample and two others is shown in Fig. 2. Although we could not go above 14 kbar at low T with our ap-

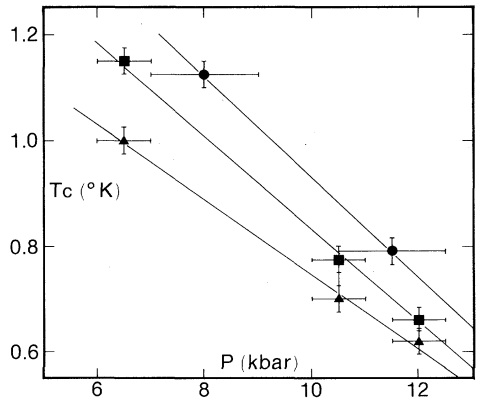

FIG. 2. Pressure dependence of T_c for three different samples (solid circles, solid squares, and solid triangles). T_c is defined at point $R = \frac{1}{2} R_n$.

paratus, the decrease of T_c with P is clear. We find $dT_c/dP = (-8 \pm 1) \times 10^{-5}$ K/bar. This negative pressure variation of T_c is unusually large, exceeding by more than a factor of 2 that of any elemental superconductor. It is similar to the T_c variation found in the anisotropic superconductor $TaSe_3$,[10] but differs in sign from that found in $NbSe_3$ and $(SN)_x$.

We believe that our results are qualitatively inconsistent with the idea that strong superconducting fluctuations occur above T_c in $(TMTSF)_2PF_6$. If 1D fluctuations were present, then a model of weakly coupled superconducting filaments should apply (i.e., $\xi_\perp <$ fiber size). For this model Deutscher, Imry, and Gunther[11] showed

$$1/T_c \sim 1/T_{c0} + 0.1N(\epsilon_F)/CT_{c0}^2. \quad (1)$$

Here T_{c0} is the transition temperature in the strong-coupling limit, and C is a measure of the coupling between filaments. As pressure is increased, we expect C to increase, and hence T_c should increase toward the value T_{c0}. However, we observe only a large decrease in T_c with increasing pressure.

The observation[8] of a large, positive transverse magnetoresistance (TMR) below 20 K has been taken as evidence[1] for superconducting fluctuations. The magnetoresistance which we observe under pressure is large but smaller than found at ambient pressure. Moreover, we find that the TMR is strongly orientation dependent. Both of these results suggest that the TMR results from a high mobility of normal electrons and an anisotropic Fermi surface. Our preliminary Hall measurements[7] give a mobility greater than 10^4 cm^2/V·sec at 4.2 K. We note that in the mercury chain compound $Hg_{3-\delta}AsF_6$ both an absence of residual resistivity (such as shown in Fig. 1 inset) and a large TMR are found and have been shown to result from an anisotropic Fermi surface.[12]

A perhaps less convincing but noteworthy argument is shown by the dashed curve in Fig. 1. This is the T dependence of the resistance at $H = 41$ kOe normalized to the $H = 0$ data at 4.2 K. Since we expect the large H field to destroy any superconducting fluctuations, the near identity of the two curves appears to rule out any large fluctuations at $H = 0$. Of course, it is always possible that $\Delta\rho(H)$ varies with T in a fortuitous manner, such that the fluctuations are masked. We feel this is very improbable.

The pressure variation of T_c can be discussed using the approximate relation $T_c = \langle\omega\rangle \exp[-(1 + \lambda)/\lambda]$. Here $\lambda = N(\epsilon_F)\langle I^2\rangle / M\langle\omega^2\rangle$ is the dimensionless electron-phonon coupling constant, $\langle I^2\rangle$ is the Fermi surface average of the electron-phonon matrix element and $\langle\omega\rangle$ is the average phonon energy. Two mechanisms can be considered which would lead to a decreased λ, and hence decreased T_c, under pressure. Either $\langle\omega^2\rangle$ is enhanced or $N(\epsilon_F)\langle I^2\rangle$ is decreased. Without other measurements we cannot know exactly how $N(\epsilon_F)\langle I^2\rangle$ will change with pressure. In other low-dimensional superconductors, a rather large change in $N(\epsilon_F) \times \langle I^2\rangle$ was required to explain $\Delta T_c/\Delta P$ since the lattice was hard.[10] Here if we assume $N(\epsilon_F)\langle I^2\rangle$ is constant the ΔT_c we observe would require $\Delta\langle\omega\rangle/\langle\omega\rangle \sim 10\%$. This is a reasonable variation for a soft lattice such as found in organic charge-transfer crystals.

In summary, we find that T_c decreases with pressure in $(TMTSF)_2PF_6$ which appears to rule out any contribution of superconducting fluctuations to the conductivity. The decrease in T_c can be qualitatively explained by a hardening of the lattice modes. Finally, we observe a novel coexistence of superconductivity and a metal-insulator transition (with associated SDW ground state) which is currently under detailed investigation.

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Localization in Disordered Two-Dimensional Systems

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The question of localization is examined by employing the localization function method in the limit of infinitesimal disorder for a square-lattice tight-binding model. Within numerical accuracy we find that the localization function equals to 1 within the band; this strongly indicates that all eigenstates become localized for nonzero disorder.

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Recently there has been considerable discussion about the existence or nonexistence of extended electronic states in two-dimensional (2D) disordered systems.[1]

The purpose of this paper is twofold. First we present two theorems concerning the localization function method,[2] $L(E)$, which is based on Anderson's original approach[3,4]; these theorems are very useful because they allow the elimination of some additional approximations associated with the $L(E)$ method. Second, we report results for the $L(E)$ function in a 2D system with infinitesimal disorder. The localization function $L(E)$ which is less (more) than one in the regions of the spectrum consisting of localized (propagating) eigenstates is given by

$$L(E)=\lim_{N\to\infty}\Big|\sum_j V^{N+1}t_j^{(N)}(E)\Big|^{1/N}=\lim_{N\to\infty}\Big|\sum_j V^{N+1}G_{n_1}^{0}G_{n_2}^{0,n_1}\cdots G_{n_N}^{0,n_1,\ldots,n_{N-1}}\Big|^{1/N}, \tag{1}$$

where V is the off-diagonal matrix element V_{ij} of the tight-binding Hamiltonian

$$H=\sum_i \epsilon_i |i\rangle\langle i| + \sum_j{}' V_{ij}|i\rangle\langle j|,$$

and

$$G_{n_i}^{0,n_1,\cdots}(z)=\langle n_i|(z-H^{0,n_1,\cdots})^{-1}|n_i\rangle; \tag{2}$$

the superscripts $0, n_1, \ldots$ denote that $\epsilon_0=\epsilon_{n_1}=\cdots=\infty$. Finally the summation over j in Eq. (1) is over all sets of sites $\{n_1, n_2, \ldots, n_N\}$ which form self-avoiding paths starting and ending at site 0.

The calculation of $t_j^{(N)}\equiv G_{n_1}^{0}\cdots G_{n_N}^{0,n_1,\ldots,n_{N-1}}$ is greatly facilitated by two theorems for $t_j^{(N)}(z)$, which are stated below (the proofs will be presented elsewhere): Theorem 1 states that

$$t_j^{(N)}(z)=\prod_i (z-\tilde{E}_i^{\,j})/\prod_i (z-E_i), \tag{3}$$

where $\tilde{E}_i^{\,j}$ are the eigenvalues of $H^{0,n_1,\ldots,n_N}$ and E_i are the eigenvalues of H^0; the proof is based on the fact that the poles of each G in the $t_j^{(N)}(z)$ are canceled by the zeros of the previous G. Theorem 2 states that

$$t_j^{(N)}(z)=\det\{G_j^{(N)}\}/G_{00}, \tag{4}$$

where the elements of the matrix $G_j^{(N)}$, G_{nm}, are the Green's functions $G_{nm}=\langle n|(z-H)^{-1}|m\rangle$, and the sites n, m belong to the self-avoiding path j. Equation (4) is valid for both open and closed self-avoiding paths. Theorem 2 is proved either by induction or by starting from Theorem 1. Up to now $t_j^{(N)}(z)$ was approximated by $(G_{n_1}^{0})^N$ in order to avoid the very tedious calculations of Green's functions with many sites excluded. Equation (4), which expresses $t_j^{(N)}$ in terms of Green's functions with no sites excluded, greatly simplifies the calculation of $t_j^{(N)}$ and makes the approximation $t_j^{(N)}\approx(G_{n_1}^{0})^N$ unnecessary. In the present case of infinitesimal disorder, G_{nm} are the periodic Green's functions, which can be calculated very accurately; thus we avoid here another usual source of approximation, namely that of replacing G_{nm} by an appropriate average (e.g., the coherent-potential-approximation average).