

Magnetic-Field-Induced Transition and Quantum Oscillations in Tetramethyltetraselenafulvalenium Perrhenate, $(\text{TMTSF})_2\text{ReO}_4$

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We report magnetoresistance measurements in $(\text{TMTSF})_2\text{ReO}_4$ which give evidence for a magnetic-field-induced transition. We also find Shubnikov-de Haas oscillations above and below the field-induced transition—a result not explained by recent theories of this novel transition.

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The $(\text{TMTSF})_2X$ family of organic charge-transfer salts has many novel properties. At room temperature, these salts are metals; at low temperature, they exhibit a diversity of ground states. Depending on the anion X , the pressure, and the cooling rate, one observes a superconducting state, an insulating spin-density-wave (SDW) state, or an anion-order (AO)-induced charge-density-wave (CDW) state.¹ Perhaps the most remarkable phenomenon found in these materials is a metal-to-semimetal transition induced by the *orbital* effect of an external magnetic field. This field-induced transition (FIT) was first observed at low temperatures in the $X=\text{PF}_6^-$ salt² and later in the $X=\text{ClO}_4^-$ salt.^{3,4} At a fixed temperature, an increase of the magnetic field (along the c^* crystal direction) leads to a threshold field, above which a series of large changes in the resistivity,²⁻⁴ the Hall effect,^{5,6} the magnetization,⁷ and the specific heat⁸ are observed. These changes suggest a series of phase transitions in which the carrier density is successively decreased with increasing field. The states above the threshold field (H_{th}) are magnetic—most likely SDW states. The occurrence of this transition is quite surprising since the electronic band structure shows that there are only open orbits in the k_a-k_b plane and a small dispersion along k_{c^*} , i.e., the $(\text{TMTSF})_2X$ salts are anisotropic, two-dimensional, open-orbit metals.⁹ Until recently, there was no explanation for this unique transition; however, now four theories have been published.¹⁰⁻¹³ They all show that the Fermi surface (FS) of a two-dimensional open-orbit metal is unstable against a SDW transition in the presence of a magnetic field. The transition is second order and results from an increased one-dimensional character of the periodic electron motion along the open orbit. The metallic, open-orbit FS becomes a semimetallic, closed FS with electron and hole pockets above H_{th} . The theories differ in many details, particularly in their interpretation of the succession of transitions above the threshold field.

In this Letter, we report the first observation of a field-induced transition in $(\text{TMTSF})_2\text{ReO}_4$. Our results are unexpected for several reasons. First, we find unambiguous evidence that Shubnikov-de Haas (SdH) oscillations occur not only above H_{th} , as previously observed in $(\text{TMTSF})_2\text{ClO}_4$, but also *below* H_{th} . Moreover, the frequency of the SdH oscillation is unaffected by the threshold field and subsequent transitions. As we discuss later, these findings are not apparently explained by any of the present theories. Secondly, our observation of a FIT in the ReO_4 salt is indirect evidence for either (1) a previously unobserved SDW transition in this compound, or (2) the first example of a field-induced CDW state in the $(\text{TMTSF})_2X$ family. A field-induced CDW has been observed in graphite¹⁴ but the origin of the transition

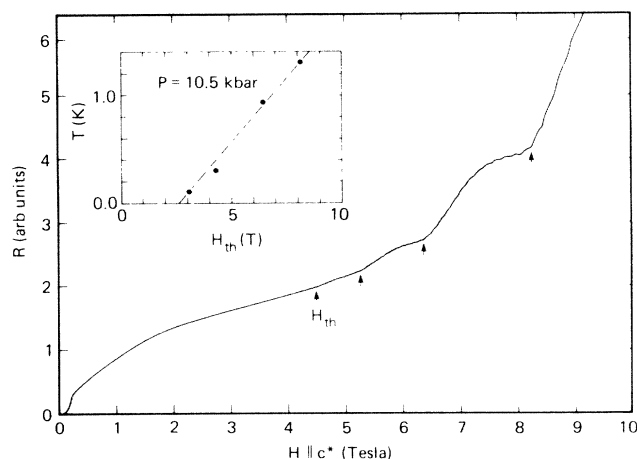


FIG. 1. The magnetoresistance of single-crystal $(\text{TMTSF})_2\text{ReO}_4$ at 300 mK and 10.5 kbar for current along a -axis and magnetic field (H) along c^* axis. The threshold field, H_{th} , and other transitions are indicated by arrows. Inset: H_{th} at various temperatures for same sample (dashed line is guide for eye).

must be different since graphite is not an open-orbit metal.

The electrical resistivity (ρ) was measured along the high-conductivity a axis with a four-probe ac technique. A He^3 cryostat was used in conjunction with a 9-T magnet and a small Cu-Be clamped pressure cell with isopentane as the pressure medium. The pressure was determined to within ± 0.5 kbar from the freezing temperature of isopentane. The samples were aligned by eye so that the magnetic field was roughly ($\pm 2^\circ$) parallel to the crystallographic c^* axis. At ambient pressure $(\text{TMTSF})_2\text{ReO}_4$ has a metal-insulator transition at 180 K driven by an ordering of the ReO_4 anions which doubles the unit cell in all directions. Above ~ 12 kbar, this AO transition is completely suppressed and superconductivity is found below $T_c \sim 1.3$ K.¹⁵ In the pressure region between ~ 9.5 and ~ 11 kbar, there is a peak in the resistivity near 50 K and superconductivity is found below $T_c \sim 1.5$ K. Both the amplitude of the resistivity peak and T_c depend in a complex manner on the cooling rate.¹⁶ In our experiments, we have used a slow cooling rate (~ 30 K/h) below ~ 120 K for all runs at pressures between 10 and 13 kbar.

The magnetoresistance of about ten $(\text{TMTSF})_2\text{ReO}_4$ samples has been measured at various temperatures and pressures. A typical result at 300 mK and 10.5 kbar is shown in Fig. 1. As the field is increased ($H \parallel c^*$) the superconductivity ($T_c = 1.4$ K) is suppressed and then at higher field a series of "transitions" appear as indicated by the arrows. We call these the "large" oscillations. The threshold field (H_{th}) can easily be seen in Fig. 1 by sighting along the curve, but it is better determined by taking the derivative of $\rho(H)$. By this method we find the dependence of H_{th} on temperature as shown in the inset to Fig. 1.

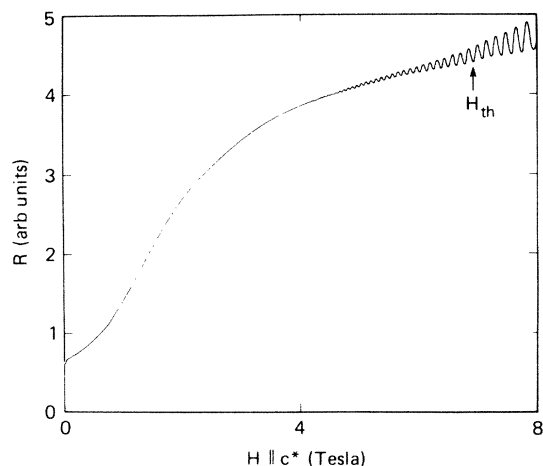


FIG. 2. The a -axis magnetoresistance of $(\text{TMTSF})_2\text{ReO}_4$ at 300 mK and 11.5 kbar. Shubnikov-de Haas oscillation is clearly visible above and below H_{th} .

At a given temperature, an increase of the pressure increases H_{th} . For example, the sample in Fig. 1 has H_{th} greater than 9 T at 12 kbar pressure. The pressure dependence of H_{th} can also be qualitatively seen by comparison among Figs. 1–3 which show $\rho(H)$ for different pressures. We observe no magnetic field hysteresis in any of these transitions. Except for the hysteresis seen⁴ in the transitions above 7 T in $(\text{TMTSF})_2\text{ClO}_4$ the above results are qualitatively similar to those found in the ClO_4 and PF_6 salts. The threshold field was determined as described above for all our data (Figs. 1–3, and other runs not included here). Note that for the ClO_4 salt it has previously been found that H_{th} determined from resistivity measurements is in good agreement with that found from specific-heat studies.⁸ Thus we expect our determination of H_{th} by the resistivity to also be accurate for the ReO_4 salt.

Our most significant new result is shown in Figs. 2 and 3. Here we see clear evidence for a set of "small" magnetic oscillations. The index number (N) of the maxima in these oscillations is plotted against $1/H$ in the inset to Fig. 3 and yields a straight line characteristic of the SdH effect with a frequency of 330 ± 15 T. It is clear from Figs. 2 and 3 that the SdH oscillations occur above and below H_{th} (indicated by the arrow) and that the oscillation frequency is unaffected by H_{th} or the higher-field transition. The SdH oscillations are difficult to see when H_{th} is low (as in Fig. 1 where they are weakly superimposed on the large oscillations). However, we see them in most samples when H_{th} is increased by temperature or pressure. The amplitude of the oscillations (large and small) is dependent on temperature, pressure, and sample quality.

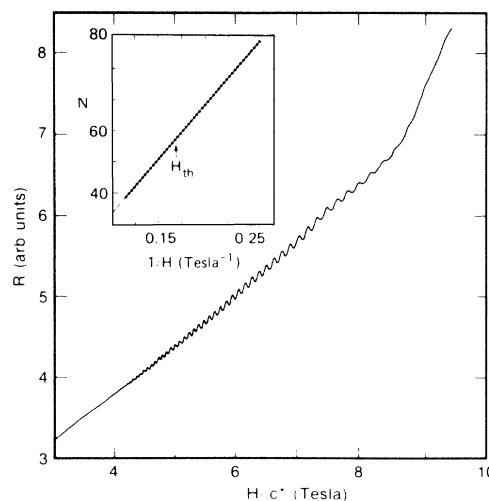


FIG. 3. The a -axis magnetoresistance of $(\text{TMTSF})_2\text{ReO}_4$ at 300 mK and 11.0 kbar. Inset: Index number of oscillation maxima against $1/H$. The straight line extrapolates to $N = 0$ at $1/H = 0$.

The data in Figs. 2 and 3 are for samples in which $\rho(T)$ smoothly decreased from 300 down to 4 K with no peak below 50 K. We take this as evidence that the ambient-pressure AO transition is essentially suppressed at pressures above ~ 11 kbar in our system.

The SdH oscillation frequency is independent of temperature and corresponds to a Fermi-surface area of approximately 4.5% of the Brillouin-zone ab plane. A nesting of the open-orbit FS with a wave vector $Q = (2k_F, 0, 0)$ would give a semimetallic FS with small pockets of about this size.⁹ A standard analysis¹⁷ of the temperature dependence of the amplitude of a particular SdH oscillation at fixed field gives an estimate of the cyclotron mass (m_c) averaged over the ab^* plane whereas the field dependence at constant temperature leads to an estimate of the Dingle temperature (T_D). We find $m_c \sim (0.35 \pm 0.05)m_e$ and $T_D \sim 1.1$ K for the sample used in Fig. 2. We do not observe either the large or small (SdH) oscillations when the magnetic field is along the b^* axis. This confirms the orbital nature of both the threshold-field transition and the oscillations.

Some significant aspects of our results are in contradiction with the present theories of the field-induced transition. The basic idea of all the theories is that an open-orbit FS is energetically unfavorable in the presence of a magnetic field. A second-order SDW transition occurs at $H_{th}(T)$ which leads to a new FS with electron and hole pockets and a SDW gap in the regions of the open orbit exactly nested by the SDW wave vector. The theories differ in their interpretation of the transitions found above H_{th} . In Refs. 11 and 12, it is suggested that the SDW wave vector is a function of temperature and field and that a series of first-order transitions occur in such a way that the electron and hole pockets change in size to keep the Landau levels always completely filled. In Ref. 13, the suggestion is that above H_{th} the system is compensated with electron and hole pockets of equal size but first-order transitions with a change in carrier density occur as the electron and hole Landau levels cross the Fermi energy with increasing field.

Our most puzzling result is the behavior of the SdH oscillations. They are clearly observed below H_{th} in many of our runs on different samples at temperatures below 1 K (see Figs. 2 and 3). They have no obvious threshold but grow smoothly out of the magnetoresistance background. Moreover, the frequency of the SdH oscillations does not change above H_{th} or above the higher-field transitions. If the oscillations are a result of the electron and hole pockets formed at the threshold field, they should not appear below H_{th} and they should change in frequency as the pocket size changes. In the ClO_4 salt SdH oscillations are observed^{5,18} with a similar frequency; however, they are only found at higher temperature ($T > 5$ K) and

higher field ($H > 10$ T) where it is very difficult to determine if (or at what H_{th}) the FIT occurs. They have been attributed¹⁰ to the pockets formed by the FIT in the ClO_4 salt.

In the theory of Chaikin and co-workers^{13,19} a quantum oscillation associated with open orbits might be observable below, but near, H_{th} . They show that for $\Delta \ll \hbar\omega_c$ a magnetic oscillation given by $n\hbar\omega_c \sim \epsilon_F$ is possible, where 2Δ is the SDW gap and $\omega_c = k_F b e H / m^* c$, b the lattice constant, c the speed of light, and k_F the Fermi wave vector. Taking m^* equal to our measured cyclotron mass ($m_c \sim 0.35m_e$) and $\epsilon_F \sim 2900$ K,⁹ we obtain a SdH frequency of about 320 T, amazingly close to our experimental result. However, this open-orbit SdH oscillation should disappear above H_{th} at low temperature where the SDW gap is well established. This is contrary to our results in the ReO_4 salt.

The SdH oscillations could result from a new ordering of the ReO_4 anions under pressure. If the anion ordering doubled the unit cell in only the a direction [$Q = (2k_F, 0, 0)$ or $(\frac{1}{2}, 0, 0)$] then a semimetal with pockets of about the right size is produced. However, if this type of AO occurs, it is difficult to understand how the magnetic field then induces another transition since the open-orbit metal no longer exists. A significant modification of the present theory would be necessary.

One might imagine that perhaps only a portion of the sample is $(\frac{1}{2}, 0, 0)$ ordered. In this case one might then expect to see SdH oscillations from the $(\frac{1}{2}, 0, 0)$ pockets and a threshold field from the unordered part of the sample. However, there is no prior experimental or theoretical evidence for this type of partial order and we will not consider it further. We also note that a partial $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ordering would not produce SdH oscillations but would merely increase the resistance below the ordering temperature. It has been speculated that under pressure, the anion ordering doubles the unit cell only along the b direction. This gives the same low-temperature ground state as found in the ClO_4 salt and a FS with two pairs of open-orbit sections with a small superlattice gap between the orbits within each pair. The SdH oscillations could arise from magnetic breakdown across the superlattice gap; however, this oscillation should disappear above the FIT when the FS forms electron-hole pockets.

The observation of a field-induced transition in the ReO_4 , ClO_4 , and PF_6 salts of TMTSF gives credence to the basic idea of the theory, i.e., that the 2D open-orbit FS is unstable in the presence of a magnetic field along c^* . However, much of the magnetoresistance data differs among the three salts and is not clear how, or whether, to modify the present theory to explain these differences. For example, the positions of large oscillations are temperature independent, have no hys-

teresis in field, and are periodic in $1/H$ in the ReO_4 and PF_6 salts; in the ClO_4 salt these oscillations are temperature dependent, have strong hysteresis, and are not periodic in $1/H$. The small, SdH oscillations have been found in the ClO_4 and ReO_4 salts but not in the PF_6 salt. It is reasonable to believe that SdH oscillations are possible in the PF_6 salt but have a small amplitude in the magnetic field, temperature, and sample purity ranges measured to date.

Finally, we note that our observation of a FIT in the ReO_4 salt suggests that a SDW state can also occur in this salt. This should be verified by measurements that directly probe the magnetism in the field-induced state. If no magnetism is detected, then we may have the first example of a field-induced CDW state in the $(\text{TMTSF})_2\text{X}$ salts.

In conclusion, we have observed SdH oscillations that occur *above* and *below* the onset of a field-induced second-order transition in $(\text{TMTSF})_2\text{ReO}_4$. The frequency of the SdH oscillation is unchanged by the transition. These results seem to have no clear explanation in the present theory of the field-induced transition. We pointed out some of the similarities and differences in the magnetoresistance behavior of the FIT in the ReO_4 , ClO_4 , and PF_6 salts. Modification of the theory will be necessary to explain our new results and to correlate them with existing Hall-effect, magnetization, and resistivity results in all these materials.

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theory of the field-induced transition.

¹See proceedings of two low-dimensional metals conferences, *J. Phys. (Paris), Colloq.* **44** (1983), and *Mol. Cryst. Liq. Cryst.* **119** (1985).

²J. F. Kwak, J. E. Schirber, E. M. Engler, and R. L. Greene, *Phys. Rev. Lett.* **46**, 1296 (1981).

³J. F. Kwak, J. E. Schirber, E. M. Engler, and R. L. Greene, *Mol. Cryst. Liq. Cryst.* **79**, 121 (1981).

⁴K. Kajimura *et al.*, *Solid State Commun.* **44**, 1573 (1982).

⁵P. M. Chaikin *et al.*, *Phys. Rev. Lett.* **51**, 2333 (1983).

⁶M. Ribault *et al.*, *J. Phys. (Paris), Lett.* **45**, L395 (1984).

⁷M. J. Naughton *et al.*, *Phys. Rev. Lett.* **55**, 969 (1985).

⁸F. Pesty, P. Garoche, and K. Bechgaard, to be published.

⁹P. M. Grant, *Phys. Rev. Lett.* **50**, 1005 (1983), and *J. Phys. (Paris), Colloq.* **44**, 847 (1983).

¹⁰L. P. Gor'kov and A. G. Lebed, *J. Phys. (Paris), Lett.* **45**, L433 (1984), and *Mol. Cryst. Liq. Cryst.* **119**, 73 (1985).

¹¹M. Heritier, G. Montambaux, and P. Lederer, *J. Phys. (Paris), Lett.* **45**, L533 (1984).

¹²K. Yamaji, *J. Phys. Soc. Jpn.* **54**, 1034 (1985).

¹³P. M. Chaikin, *Phys. Rev. B* **31**, 4770 (1985).

¹⁴Y. Iye *et al.*, *Phys. Rev. B* **25**, 5478 (1982).

¹⁵S. S. P. Parkin, D. Jerome, and K. Bechgaard, *Mol. Cryst. Liq. Cryst.* **79**, 213 (1982).

¹⁶S. Tomic, D. Jerome, and K. Bechgaard, *Mol. Cryst. Liq. Cryst.* **119**, 241 (1985), and *J. Phys. C* **17**, L11 (1984).

¹⁷L. M. Roth and P. N. Argyres, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 1, p. 159.

¹⁸J. P. Ulmet, P. Auban, and S. Askenazy, *Solid State Commun.* **52**, 547 (1984).

¹⁹P. M. Chaikin, T. Holstein, and M. Ya. Azbel, *Philos. Mag. B* **48**, 457 (1983).