# Toward a Unified Phase Diagram in $(TMTSF)_2X$

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We have made a detailed pressure–magnetic-field–temperature phase diagram study of the organic conductors $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ in the low temperature regions dominated by the cascade of field-induced spin density wave (FISDW) transitions. The $PF_6$ salt shows general agreement with the "standard model" for the FISDW and the pressure dependence of its high field insulating state connects nicely with the $n=0$ SDW. The $ClO_4$ salt shows agreement with the standard model only when an anion ordering transition has been suppressed above $\sim 5$ kbar.

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The Bechgaard salt family of $(TMTSF)_2X$ (where TMTSF is tetramethyltetraselenafulvalene and $X=PF_6$, $ClO_4$, $AsF_6$, $ReO_4$, ...) is notable for being the first organic superconductor [1] and for exhibiting the quantum Hall effect in a bulk crystal [2,3]. The crystal structure consists of chains of donor TMTSF molecules separated by chains of acceptor anions, resulting in an anisotropic two-dimensional conductor with bandwidths given by $4t_a:4t_b:4t_c = 1:0.1:0.003$ eV. The in-between dimensionality of the system allows for a rich phase diagram as pressure, magnetic field, temperature, and the anion are varied. Above 6 kbar $(TMTSF)_2PF_6$ exhibits the integral quantum Hall effect (QHE) and a cascade of field-induced spin density wave (FISDW) transitions. $(TMTSF)_2ClO_4$ at ambient pressure has a much more complex phase diagram with FISDW's, an extremely stable semimetal phase [4], reentrance to a metallic state [5], and a controversial insulating phase above 27 T [6]. In order to better understand the similarities and differences between these two salts, we have measured the pressure–magnetic-field–temperature ($P$-$H$-$T$) phase diagram of both $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ up to 30 T in magnetic field and up to 16 kbar of pressure.

As the prototypical member of the family, $(TMTSF)_2PF_6$ is metallic at room temperature and exhibits a transition to spin density wave (SDW) insulator at 12 K at ambient pressure. The SDW is suppressed above 6 kbar and superconductivity is observed at $\sim 1$ K. The superconductivity is suppressed with a small field (200 G) perpendicular to the conducting plane, and at much higher field ($>3$ T) a cascade of FISDW transitions to different QHE states is found. The phenomena of the FISDW, the QHE, and the phase diagram of $(TMTSF)_2X$ are currently understood as a consequence of the changing dimensionality of the system under pressure and magnetic field [7]. A 1D metal is unstable against a density wave distortion. Pressure increases the dimensionality while a magnetic field decreases it. Competition between the SDW wave vector and the reciprocal of the magnetic length, $G=eHb/\hbar c$, gives rise to a cascade of FISDW transitions to QHE states with quantum numbers $n=0,1,2,3,\ldots$ (starting from high field and going toward $H=0$), where $n$ indexes the conductance of the state $\sigma_{xy}=ne^2/h$. Though the "standard model" is sufficient to describe $(TMTSF)_2PF_6$, $(TMTSF)_2ClO_4$ exhibits strong deviations. The cascade is interrupted by unexplained phases with opposite sign Hall effect, there is an apparent "$n=\frac{1}{3}$" state which is extremely stable, the normal metal reenters at high field, and at yet higher field there is a further transition to a very high field insulating state (VHFI) [4,6].

In this Letter we present the results of an extensive phase diagram study of $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$. Our initial aim was observing the behavior of the different phases as pressure increased the bandwidths and dimensionality. In fact our observations confirm the accepted picture—the FISDW transitions are all pushed to higher field as pressure increases. Serendipitously, we also stumbled across some observations which begin to make the behavior of the $ClO_4$ salt understandable. The anion ordering transition which occurs at ambient pressure at 24 K in the $ClO_4$ salt is absent for pressures above 5 kbar. Correspondingly, the FISDW phase boundary changes discontinuously through this pressure, exhibiting complex behavior below 5 kbar and standard-model-$PF_6$-like features above. We therefore have experimental evidence for the generally held belief that the anion ordering is responsible for the differences in these materials.

The details of the experiment are found in Ref. [3]. For the experiments on $(TMTSF)_2ClO_4$ the samples were cooled more slowly than 7 mK/min through the anion ordering transition region to achieve a very well relaxed state.

The pressure–magnetic-field–temperature phase diagram of $(TMTSF)_2PF_6$ is presented in Fig. 1. The SDW transition temperature decreases under increasing pressure, and superconductivity (SC) appears above 6 kbar. Essentially at the critical pressure, 6 kbar, the SDW transition occurs prior to the superconductivity and the SDW insulating phase is restored immediately above the SC critical field. It is interesting to note that the transition temperature increases smoothly with magnetic field with

 

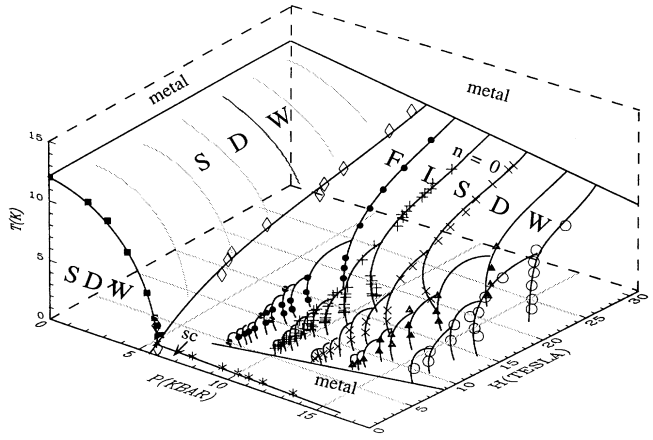


FIG. 1. Pressure–magnetic-field–temperature phase diagram of $(TMTSF)_2PF_6$. The lines are guides to eye.

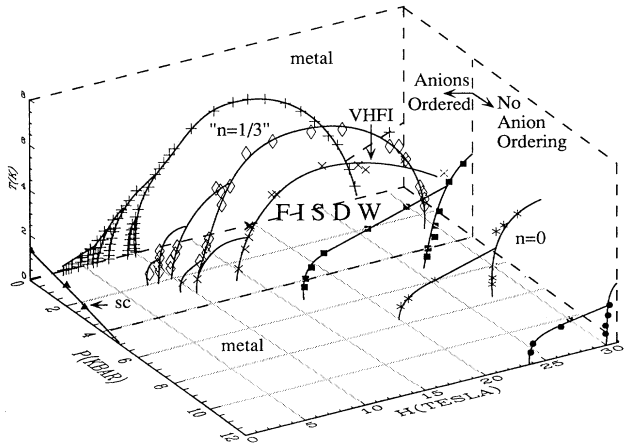


FIG. 2. Pressure–magnetic-field–temperature phase diagram of $(TMTSF)_2ClO_4$.

no structure in the phase boundary here. Above the critical pressure the cascade of FISDW transitions is observed above a finite threshold field. A series of transitions is observed under increasing magnetic field, leading to a most remarkable phase diagram. The cascade of transitions persists until the system enters the insulating $n=0$ FISDW state. The cascade of FISDW culminating in the $n=0$ state seems to be the universal behavior in $(TMTSF)_2PF_6$ up to the 30 T of magnetic field. The FISDW fields are very pressure dependent as are the number of transitions at each pressure. Whereas at 8 kbar there are over eleven distinguishable transitions, there are only five transitions at 16 kbar. The initial threshold field increases from 4.5 T at 8 kbar to 8 T at 16 kbar. A similar increase is observed for the final $n=0$ transition as it increases from about 16 to 24 T between 8 and 16 kbar.

The $P$-$H$-$T$ phase diagram of $(TMTSF)_2ClO_4$ is shown in the Fig. 2. The ambient (zero) pressure phase diagram of $(TMTSF)_2ClO_4$ consists of superconductivity and the cascade of FISDW transitions similar to $(TMTSF)_2PF_6$ above 6 kbar of pressure. The notable difference is the reentrant behavior in the phase diagram followed by a transition to the VHFI phase above 27 T. The phase diagram exhibits greater pressure dependence in $(TMTSF)_2ClO_4$ than in $(TMTSF)_2PF_6$. Even without the divisions we have indicated on the phase boundary, it is clear that the behaviors above and below 4 kbar are substantially different. In the low pressure studies there are a number of transitions preceding a wide phase (labeled "$n=\frac{1}{3}$") whose transition temperature reaches a maximum and then decreases with increasing field. The entire phase boundary in this region, including the reentrance and the VHFI transition, shifts to higher field as the pressure is increased. The VHFI phase is quickly pushed out of the accessible field regime, even though the reentrant behavior is still observed for $P<3$ kbar. Only the "Ribault anomaly" (negative Hall step) [8] and the $n=1$ and "$n=\frac{1}{3}$" phases are observable under 3 kbar of pressure.

Above 5 kbar, we observe only two phases and a constantly increasing transition temperature with field. The lower field phase is semimetal while the "new" phase is insulating. Further increasing pressure shifts these structures to higher field. The most direct evidence for the new phase comes from the results of the Hall effect.

The Hall effect of $(TMTSF)_2ClO_4$ for various pressures at 0.5 K is presented in Fig. 3. Under ambient pressure, the sequence of transitions culminates in the $n=2$, the Ribault anomaly, the $n=1$, and finally the "$n=\frac{1}{3}$" state above 6 T. Above 27 T, the transition to the VHFI causes the resistance to grow so rapidly that the evaluation of $\rho_{xy}$ is difficult. At 3 kbar of pressure, most of the low field FISDW's are removed and the Ribault anomaly is considerably weakened (it is not visible in Fig. 3 without magnification of the $y$ axis). Although the value of the "$n=\frac{1}{3}$" plateau is lower than at 1 bar, this may be the result of sample geometry. What is more disturbing is that the ratio of $\rho_{xy}$ "$n=\frac{1}{3}$" to "$n=1$" is

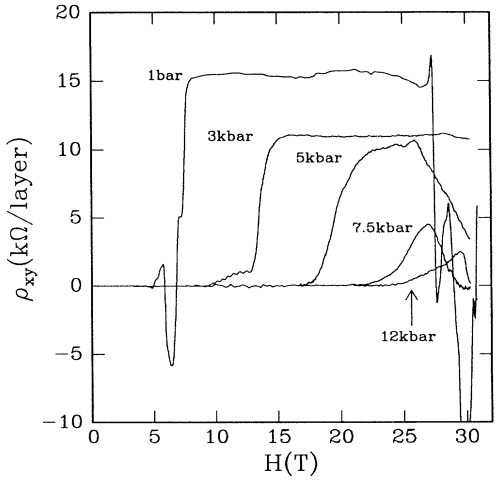


FIG. 3. Hall effect of $(TMTSF)_2ClO_4$ for various pressure.

much greater than 3 and hence not universal with pressure. (It is not likely that the temperature is too high for the full establishment of the "$n=1$." Measurements were subsequently done down to 50 mK.)

At 5 kbar and above, $\rho_{xy}$ shows at most a single plateau before it is cut off by a transition to a state where the Hall coefficient approaches zero. The longitudinal resistance increases sharply at this transition suggesting that the new phase is insulating.

A real clue as to what is going on is found in the resistance versus temperature on cooling through the 24 K range of the ambient pressure anion ordering transition. The signature of the anion ordering is a "cusp," an abrupt slow change in $R$ vs $T$. We observe this cusp at 1 bar, 2 kbar, and 3 kbar at $\sim 24$ K, but it is not present at any pressure above 5 kbar. This suggests that above 5 kbar there is no anion ordering. Stronger proof of the absence of anion ordering comes from the angle of the dominant "Lebed resonance" in the magnetoresistance, which shows no doubling of the unit cell in the $b$ direction [9,10].

The $P$-$H$-$T$ phase diagram of $(TMTSF)_2PF_6$ can be understood in terms of changing dimensionality of the system [7,11]. Under the framework of the "standard model," the phenomenon of FISDW comes about as a consequence of the relative proximity to the SDW under pressure and the restoration of the SDW by magnetic field. Parameters relevant in determining the overall shape of the phase diagram involve $t_b'$ and $t_c'$, the unnested band integrals along the $b$ and $c$ directions, respectively. Pressure increases the effective dimensionality of the system by increasing the electronic overlap, and the system is perturbed away from perfect nesting. When $t_b'$ is greater than $t_b'^*$, the critical unnested band integral, the system no longer gains energy from the SDW formation, and the SDW is suppressed [11]. In the phase diagram for $(TMTSF)_2PF_6$ the SDW state below the superconducting critical pressure of 6 kbar may be described as the region where $t_b' < t_b'^*$, and the FISDW states above 6 kbar may be characterized as the region where $t_b' > t_b'^*$.

Magnetic field undoes the effect of pressure. Application of magnetic field makes the electronic motion more one dimensional and the SDW is restored [7]. The energy of the system is lowered by the Landau quantization of the carrier pockets formed by imperfect nesting. $E_F$ lies in a gap between Landau levels and this results in the QHE. Increasing the field produces the cascade of FISDW's with decreasing quantum numbers. As the pressure is increased $t_b'$ increases and it takes appropriately larger fields to undo its effects. When the cyclotron energy is greater than $t_b'$, the system enters the $n=0$ FISDW state and is fully restored to the ambient pressure SDW. The $n=0$ FISDW state under pressure and magnetic field should be the same phase as the ambient pressure SDW. Many of these effects are apparent in Fig. 1. *It is particularly striking that at a field of 30 T the SDW transition temperature versus pressure is essentially a continuous curve.* So passing from SDW to $N=0$ looks like staying in the same phase. The condition for FISDW instability, on the other hand, is that the cyclotron energy be greater than $t_c'$ so that Landau bands do not overlap. Consequently, the SDW threshold field and the $n=0$ transition are directly related to $t_c'$ and $t_b'$, respectively.

In a most simple approximation, $t_b'$ and $t_c'$ change linearly with pressure, and the $n=0$ transition and the threshold field should also change linearly with pressure. Experimentally, both the $n=0$ transition field and the threshold field increase at roughly 1 T/kbar between 8 and 16 kbar. This behavior is consistent with changing dimensionality of the system and with theoretical estimates of Yamaji [12]. The reduction in the number of FISDW subphases under increasing pressure is a consequence of increasing dimensionality as well. With an increase in $t_c'$, the energetic gain necessary to restore the SDW becomes possible only with lower quantum number FISDW's under higher magnetic field.

Another consequence of the standard model is that the transition fields into the states with quantum number $n$ and $\rho_{xy}=h/ne^2$ are given by $H_n=H_0/(\alpha+n)$. For the $(TMTSF)_2PF_6$ data this expression works very well with $\alpha=3.5$.

We now turn our attention to $(TMTSF)_2ClO_4$. At high pressure we do not have many phases to play with, but there is nothing in the phase diagram to suggest disagreement with the standard model. In particular there is an insulator at high field and a semimetal phase just below it. If we assign these phases as $n=0$ and $n=1$ then we find that they agree with the $H_n$ rule above, again with $\alpha=3.5$. So above 5 kbar things are okay. *In the absence of anion ordering $(TMTSF)_2ClO_4$ works with the standard model.*

We should not expect an extrapolation through the discontinuous change brought on by the anion ordering to work, but suppose we try it anyway. In Fig. 4 we show the low temperature cut of the phase diagram. It is somewhat reasonable from the previous figures to take

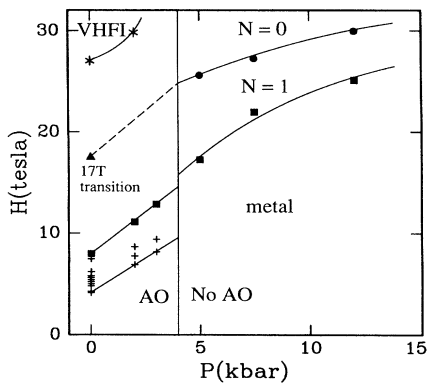


FIG. 4. Pressure–magnetic-field slice of $(TMTSF)_2ClO_4$ phase diagram at low temperature.

the $n=1$ transition above 5 kbar, to the "$n=\frac{1}{3}$" below. However, the $n=0$ at high pressure does not extrapolate to a distinct phase at low pressure. It does extrapolate to the vicinity of $\sim 17$ T where many anomalies have previously been seen in a number of measurements. If extrapolation makes any sense, then "$n=\frac{1}{3}$" is really $n=1$ [13] and $n=0$ is strongly suppressed by the anion ordering.

A recent model by Osada, Kagoshima, and Miura has precisely these features [14]. It suggests that the anion ordering (which causes a dimerization in the $b$ direction and splits the single band into two bands with different Fermi wave vectors) has a profound effect on the FISDW's. In particular, the model suggests that the gap from the anion ordering has virtually no effect on the odd $n$ states but strongly suppresses the even $n$ states. If we start in the $n=1$ state and lower the field we should end up in the $n=3$ phase. The old $\frac{1}{3}$:1:2:3 states would then become 1:3:5:7. (This would explain the ratio in Hall resistances between highest field semimetal states, but not the others.) The extreme stability of the $n=1$ state would come from the strong suppression of the $n=0$ state, but eventually at high enough field the $n=0$ is predicted to be more favorable. Within this model, the reentrance comes from the suppression of the $n=0$ and the VHFI state is the $n=0$ state. This model also suggests that the VHFI transition should oscillate with field.

While the basic ideas of this model are very appealing and may be correct, the model awaits some crucial testing. It relies on a sizable anion ordering gap and this in turn relates the suppression of the $n=0$ phase to the amplitude of phase boundary oscillations of this phase. As yet we have no evidence of an oscillating phase boundary in any of the high field phases. The predicted reentrance region is much smaller than seen experimentally. If the 17 T anomaly is associated with the suppressed $n=0$ transition then it should extrapolate to the VHFI, which it does not appear to. The Hall ratios aside from 1:3 do not work. On the other hand these may be minor points related to details of band structure, etc.

In conclusion, we find that the $PF_6$ salt behaves in almost total accord with the standard model for the FISDW and its pressure dependence clearly shows that the insulating FISDW state and the zero field SDW are continuous. We have also found that it is possible to suppress the anion ordering transition in $(TMTSF)_2ClO_4$ by the application of pressure greater than $\sim 4$ kbar. Without anion ordering the $ClO_4$ salt exhibits FISDW behavior similar to other Bechgaard salts in particular showing the $n=0$ transition for the first time. The complex behavior caused by the anion ordering is generally in accord with a recent model by Osada, Kagoshima, and Miura.

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[10] The pressure dependence of the anion ordering has previously been studied by K. Murata *et al.*, Mol. Cryst. Liq. Cryst. **119**, 245 (1985), who found that anion ordering persisted up to their highest pressure, 8 kbar. We suggest that this difference rests primarily in the pressure determination, consistently $\sim 3$ kbar difference between groups. For example, the reported $P_c$ for superconductivity in $(TMTSF)_2PF_6$ is 9 kbar in Ref. [1] while we find 6 kbar.

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