Superconductivity and Magnetic-Field-Induced Spin-Density Waves

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A recent theory of the magnetic-field-induced spin-density wave (FISDW) transitions observed in the Bechgaard salts $(TMTSF)_2X$ emphasizes the role of the superconducting pairing interaction in FISDW formation. No superconductivity is observed in $(TMTSF)_2NO_3$, unlike other metallic Bechgaard salts. Our study of $(TMTSF)_2NO_3$ in pressure up to 13 kbar, temperature down to 0.5 K, and magnetic field up to 30 T shows no sign of FISDW. The "rapid" magnetoresistance oscillations observed but unexplained in other Bechgaard salts are also observed here.

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The quasi-two-dimensional organic conductors $(TMTSF)_2X$, where TMTSF is tetramethyltetraselenafulvalene and $X=PF_6^-$, ClO_4^-, ReO_4^-, etc., display a cornucopia of phenomena such as spin-density waves (SDW), superconductivity (SC), quantum Hall effects (QHE), "rapid" oscillations (RO), and anion ordering (AO) as temperature, pressure, and magnetic field are varied.[1-4] Typically these Bechgaard salts undergo antiferromagnetic SDW ordering at low temperature. Application of pressure suppresses the transition temperature of the insulating SDW state, and above a critical pressure the metallic state is stable with superconductivity often occurring near 1 K. The superconductivity is destroyed under low magnetic field, and in moderate field ($H>4$–5 T) reappearance of the SDW state, i.e., a magnetic-field-induced spin-density wave (FISDW), is found. Most remarkably, the QHE has been observed in the semimetallic FISDW state.[3,4] Recent experiments on $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ have established the quantized Hall plateaus and peaks in the magnetoresistance as salient features of the FISDW transitions.[3-5] Such results have been well corroborated by thermodynamic measurements such as magnetization[6] and specific heat.[7] Until recently the superconductivity found in all current FISDW salts was just an interesting artifact. Whereas the currently accepted theoretical model of the FISDW,[8,9] known as the "standard model," has tended to neglect the superconductivity found in all FISDW salts, it plays a nontrivial role in a recent theory proposed by Yakovenko.[10]

Within the framework of the standard model, the role of pressure is to change the band structure until the Fermi surface deviates from perfect nesting and the ambient-pressure SDW is destroyed.[9] The existence of the superconductivity is unimportant. The role of magnetic field is to undo the effect of pressure. Application of the magnetic field makes the system more one dimensional, and the nesting of the Fermi surface is enhanced, leading to a SDW instability. Thus, the key to FISDW formation in the standard model is the enhanced nesting of the Fermi surface coupled with the proximity of the SDW state at low pressure. It further predicts a cascade of transitions between QHE states with $\rho_{xy}=h/ne^2$ and finally at high field an $n=0$ SDW semiconductor. An excellent semiquantitative agreement is found with the experiments on the PF_6 salt[3,4] and on the ClO_4 salt for $H<8$ T.[2] However, in one of its greatest shortcomings, the standard model fails to predict the reentrance of the metallic state at 27 T in $(TMTSF)_2ClO_4$.[11]

In the alternate theory proposed by Yakovenko, the role of the superconducting pairing interaction is emphasized, in contrast to the Fermi-surface nesting in the standard model. He points out that in all cases where the FISDW is observed, the $H=0$ state is superconducting. The effect of the magnetic field is to renormalize the attractive interaction, which gives rise to the superconductivity, to produce an interchain electron-hole pairing interaction that results in the formation of the FISDW. At extremely high magnetic field the electrons are localized on the independent chains and the system becomes truly one dimensional. Fluctuations reduce the FISDW transition temperature and the reentrance to the metallic state is predicted. Within this model, no FISDW should be present if the zero-field state is not superconducting. A simple and direct test of Yakovenko's model is to look for FISDW in a nonsuperconducting member of the Bechgaard salts, $(TMTSF)_2NO_3$.

Being the best conductor of the family, $(TMTSF)_2$-NO_3 shares many similar features with the other FISDW salts as outlined in Table I. Under ambient pressure it undergoes an SDW-insulator transition at 12 K,[12] similar to the PF_6 salt. An anion-ordering transition along the $(\frac{1}{2},0,0)$ direction is observed at 45 K.[13] Although the metallic state is stabilized above 8 kbar, no superconductivity has been observed up to 24 kbar of pressure down to 50 mK.[14] Based on the absence of superconductivity, Yakovenko's model predicts that no FISDW should be found in $(TMTSF)_2NO_3$. On the other hand, based on the proximity of the SDW state at lower pressure, the standard model predicts that FISDW transitions should be found in $(TMTSF)_2NO_3$. The purpose of this work is to search for the FISDW in

TABLE I. A comparison of SDW transition temperature, anion ordering, anion-ordering transition temperature, superconductivity, field-induced spin-density wave, and rapid oscillations for four $(TMTSF)_2X$ Bechgaard salts.

Anion	T_{SDW} (K)	AO	T_{AO} (K)	SC	FISDW	RO
ClO_4	5[a]	$(0,\frac{1}{2},0)$	24	Yes	Yes	Yes
PF_6	12	No	···	Yes	Yes	Yes
ReO_4	20[b]	$(0,\frac{1}{2},\frac{1}{2})$	180	Yes	Yes	Yes
NO_3	12	$(\frac{1}{2},0,0)$	45	No	No	Yes

[a]Only for quenched samples.
[b]Under recycled pressure (Ref. 20).

$(TMTSF)_2NO_3$, to test the two models, and to clarify some of the outstanding puzzles in the Bechgaard salts.

The experiments were performed using a miniature pressure clamp. The details of the pressure apparatus are described elsewhere.[4] Because of the loss of pressure due to freezing of the pressure medium upon cooling, low-temperature pressure was determined by monitoring the superconducting transition of lead. Pressure was gradually increased until the SDW transition was completely suppressed in order to reach the metallic state. Samples were cooled very slowly through the anion-ordering transition as is typically done with $(TMTSF)_2ClO_4$. Most cooling rates through the anion-ordering transition were usually better than 50 mK/min. Although small resistance jumps, which are known to appear in all $(TMTSF)_2X$ compounds due to cracks, were observed under ambient pressure, no cracks were observed in the samples under pressure. The ambient-pressure experiment was done at Princeton University using a superconducting solenoid. The experiments under pressure were done at Princeton and the Francis Bitter National Magnet Laboratory. Resistance measurements showed that the metallic state extended down to 0.5 K and no superconductivity was observed. More than ten pressurized samples showed similar results, but the data presented in this Letter are from two samples for which the experiment was performed up to the highest magnetic field.

In Fig. 1 resistance measurements for three $(TMTSF)_2NO_3$ samples under different pressure are presented. Under ambient pressure an anion-ordering transition is observed near 45 K and shows up as a sharp drop in resistance. The SDW transition is observed near 12 K as the rapid resistance increase. The SDW transition temperature is suppressed under increasing pressure. Above 8 kbar the SDW transition is completely suppressed and the metallic state is observed. For a sample at 8.2 kbar a resistivity ratio $R(300\text{ K})/R(4.2\text{ K})$ of 100 was obtained. We observed that the AO transition temperature increases nearly up to 50 K under increasing pressure. A resistive anomaly, marked by a sharp increase in resistance, is observed at the AO transition in the samples under high pressure (see data for 13 kbar) as has been previously reported.[14] The resistive jump is sometimes absent under intermediate pressures but appears under high pressure. The magnetotransport measurements we report here were done in the metallic state.

In Fig. 2 the magnetoresistance of the two $(TMTSF)_2NO_3$ samples at 8.2 and 13 kbar is presented along with that of a PF_6 sample under 10 kbar of pressure. Above 5 T the difference between $(TMTSF)_2PF_6$

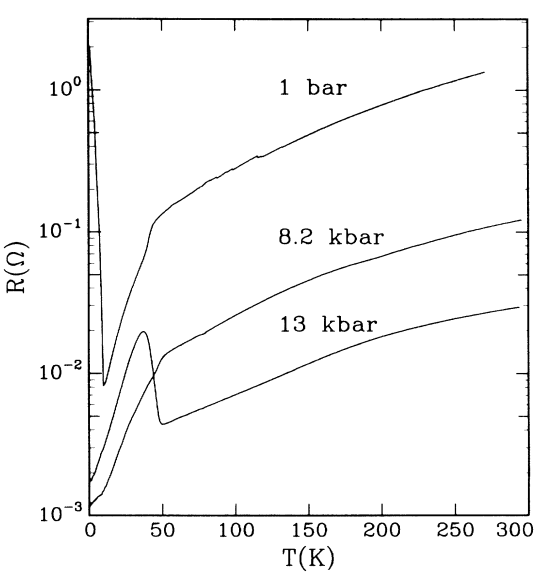

FIG. 1. Resistance measurements of $(TMTSF)_2NO_3$ for various pressures. A slight increase in the AO transition temperature is observed under pressure. No superconductivity is observed down to 0.5 K.

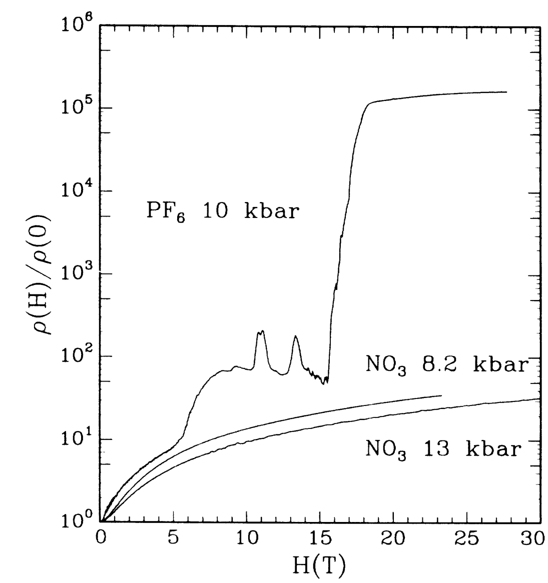

FIG. 2. Magnetoresistance of two $(TMTSF)_2NO_3$ samples under 8.2 and 13 kbar, respectively, shown along with that of a $(TMTSF)_2PF_6$ sample under 10 kbar at $T=0.5$ K. Whereas FISDW transitions appear in $(TMTSF)_2PF_6$ above 5 T, no FISDW transitions are observed in $(TMTSF)_2NO_3$ up to 30 T.

and $(TMTSF)_2NO_3$ is striking. The $(TMTSF)_2PF_6$ exhibits the cascade of FISDW's as increases and peaks in resistance whereas the $(TMTSF)_2NO_3$ shows a monotonically increasing magnetoresistance up to 30 T with no sign of the FISDW. A relatively large magnetoresistance is observed in $(TMTSF)_2NO_3$ with a ratio $\rho(30\ \mathrm{T})/\rho(0\ \mathrm{T})$ of about 30. A similar magnetoresistance is observed in the normal state below 5 T in the PF_6 sample. But in the NO_3 salt we do not observe the 4 orders of magnitude increase in magnetoresistance brought on by the FISDW transitions between 5 and 16 T nor any QHE-like behavior shown by large peaks in magnetoresistance. The FISDW transition is conspicuously absent in nearly a dozen $(TMTSF)_2NO_3$ samples that we have studied.

In Table I we summarize some of the properties of four of the Bechgaard salts. All have SDW transitions which can be suppressed with pressure to obtain a low-temperature metallic state. Three exhibit anion-ordering transitions, three exhibit superconductivity, and three exhibit the FISDW. The direct correlation is between superconductivity and FISDW, lending support to Yakovenko's hypothesis. (As we will discuss later all also exhibit rapid magnetoresistance oscillations.)

An easy objection to the correlation of superconductivity and the FISDW would be that we simply have not gone sufficiently high in field. While we cannot directly disprove this possibility it is worth pointing out that minimum threshold field (for different pressures) for the FISDW's in the other salts has always been less than 10 T at 0.5 K (3 T for ClO_4, 4 T for PF_6, 6 T for ReO_4). Considering the comparable T_{SDW} it is reasonable to expect a similar threshold field, and we have searched to the highest available field, 30 T, for experiments at 0.5 K without any sign of FISDW transitions.

The absence of FISDW and superconductivity in $(TMTSF)_2NO_3$ is quite perplexing because of its similarity to other FISDW salts. The most gross difference between $(TMTSF)_2NO_3$ and other Bechgaard salts is the presence of AO at the wave vector $(\frac{1}{2},0,0)$. Whereas the centrosymmetric PF_6 anion does not order, the tetrahedral anions ClO_4 and ReO_4 are found to order along the $(0,\frac{1}{2},0)$ and $(0,\frac{1}{2},\frac{1}{2})$ directions, respectively, in the pressure regime where FISDW transitions are found. The presence of an AO transition *per se* does not diminish either the SDW or superconducting states, as shown theoretically for an SDW transition for the $(0,\frac{1}{2},0)$ direction[15] and experimentally for the ClO_4 and ReO_4 salts.

However, one might expect that an AO with wave vector $(\frac{1}{2},0,0)$ would have more dramatic effects since the distortion has a component along the most highly conducting direction. In fact, if these materials were one dimensional rather than quasi-one-dimensional, this distortion would put a gap directly at the Fermi energy and produce an insulating state. Given the bandwidths characteristic of the Bechgaard salts (t_a:t_b:t_c $\approx$ 1:0.1:0.003 eV) we would expect a small partial gap on the Fermi surface which would leave an electron and a hole pocket. It is therefore remarkable that the distortion has such a small effect at ambient pressure (see Fig. 1) where surprisingly it leads to a *decrease* rather than an increase in resistance. Nonetheless, this $(\frac{1}{2},0,0)$ distortion and small gap might inhibit the superconductivity and particularly the SDW and FISDW instabilities which prefer nesting at or near $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The best argument against this is that the ambient-pressure data for $(TMTSF)_2NO_3$ show virtually the same T_{SDW} as for $(TMTSF)_2PF_6$ which has no AO.

When sufficient pressure is applied, the resistive anomaly at the AO temperature can turn to a large resistance increase (see the 13-kbar data in Fig. 1), somewhat reminiscent of the charge-density-wave transitions in $NbSe_3$.[16] In this case we might expect the decreased density of states at the Fermi level, $N(\epsilon_F)$, to suppress both the superconducting and FISDW T_c. We note, however, that we can attain the low-temperature metallic state without any increase in the resistance at the AO transition (Fig. 1, 8.2 kbar), and no sign of superconducting or FISDW transitions were seen. Furthermore, the AO transition is not regarded as a Fermi-surface instability[17] that would require a depletion of $N(\epsilon_F)$.

One interesting feature of the data is the anomalous magnetoresistance observed in the normal state of $(TMTSF)_2NO_3$. The large magnetoresistance observed in $(TMTSF)_2NO_3$ is very much reminiscent of the normal state found in the ClO_4 and PF_6 salts as shown in Fig. 2. The high-field magnetoresistance is found to obey Kohler's rule with $\Delta\rho/\rho \sim (H/\rho)^{\alpha}$, with $\alpha \approx 1.35$ for 8.2 kbar and 1.14 for 13 kbar.

Magneto-oscillations are observed in both transport and thermodynamic quantities of the Bechgaard salts.[18] The origin of these "rapid" (compared to the frequency of the FISDW transitions) oscillations has remained a mystery since these are open-orbit metals. They are observed throughout the phase diagram in $(TMTSF)_2ClO_4$ and $(TMTSF)_2ReO_4$,[18] and in the $n=0$ state in $(TMTSF)_2PF_6$.[3,4] In $(TMTSF)_2NO_3$ the $(\frac{1}{2},0,0)$ anion ordering gives rise to a possibility of closed orbits. Thus, oscillations in magnetoresistance should be present below the AO transition. While we observe the oscillations in magnetoresistance in the ambient-pressure SDW state of $(TMTSF)_2NO_3$, a search in the metallic state above the critical threshold pressure showed no sign of rapid oscillations. In Fig. 3 the oscillations in magnetoresistance in the ambient-pressure SDW state at 1.3 K are shown. The frequency of the oscillations is 75 ± 10 T, lower than frequencies found in other salts. The occurrence of the rapid oscillations in all these salts appears with one common feature, a doubling of the cell in the **b** direction, from AO in the cases of ClO_4 and ReO_4 salts, and from the $n=0$ SDW state in NO_3 and PF_6 salts. Thus, the quantum interference mechanism[19] may be responsible for the rapid oscillations in the Bechgaard salts.

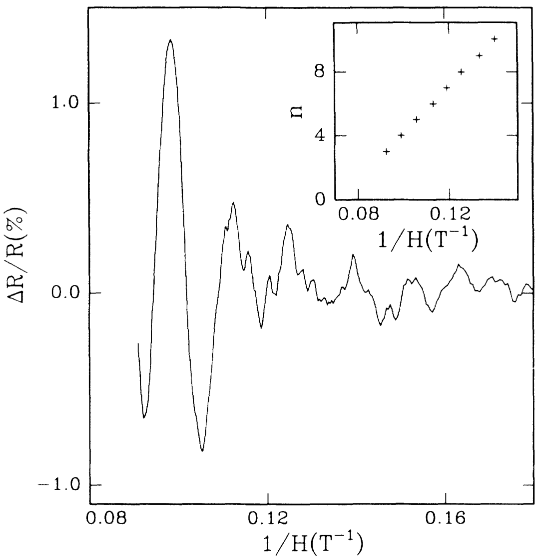

FIG. 3. Relative amplitude of magnetoresistance oscillations vs inverse field at $T=1.3$ K. Inset: Index of oscillation peaks in the magnetoresistance vs inverse field.

In summary, we have performed magnetotransport measurements of a nonsuperconducting member of the Bechgaard salts, $(TMTSF)_2NO_3$. The standard model predicts that $(TMTSF)_2NO_3$ *will* exhibit an FISDW since its low-pressure phase is an SDW. Yakovenko's model predicts that $(TMTSF)_2NO_3$ *will not* exhibit an FISDW since its low-field phase is not superconducting. *We find no FISDW in* $(TMTSF)_2NO_3$. The models are fundamentally incompatible. We must find a way to combine the tremendous successes of the standard model in describing the QHE and cascade of transitions with the successes of Yakovenko's predictions for $(TMTSF)_2NO_3$ and for the high-field reentrance in $(TMTSF)_2ClO_4$. If not, we must find a reason for the lack of both superconductivity and FISDW particular to $(TMTSF)_2NO_3$. Finally, rapid oscillations are also observed in the $n=0$ SDW state of $(TMTSF)_2NO_3$.

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