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Magnetothermopower study of $(TMTSF)_2PF_6$ (where TMTSF is tetramethyltetraselenafulvalene)

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We have performed a thermoelectric-power study of the organic conductor $(TMTSF)_2PF_6$ which exhibits a type of bulk quantum Hall effect (QHE), resulting from a cascade of magnetic-field-induced spin-density-wave (FISDW) transitions. The FISDW are characterized by a sharp increase in thermopower as the temperature is lowered through the transition temperature, followed by an exponential decrease as temperature approaches zero. This suggest a temperature-dependent gap leading to collective QHE-like transport. Most surprising is the vanishing thermopower in the insulating "n=0" state.

It was recently reported that the quantum Hall effect (QHE) has been observed in the quasi-two-dimensional *bulk* organic conductor $(TMTSF)_2PF_6$ where TMTSF is tetramethyltetraselenafulvalene.[1,2] Whereas the conventional QHE arises as an interplay of noninteracting particles with disorder and magnetic field, the QHE in the Bechgaard salts is a consequence of many-body interactions that lead to a collective spin-density wave distortion.[3] To study the *unconventional* QHE of the magnetic-field-induced spin-density waves (FISDW's), we have performed thermoelectric power measurements on $(TMTSF)_2PF_6$.

The Bechgaard salt group has shown an array of various broken-symmetry ground states within the accessible laboratory range of pressure, temperature, and magnetic field: superconductivity, spin-density wave (SDW), QHE, anion ordering, anomalous magneto-oscillations and so on.[4–6] The most fascinating and intriguing phenomenon in the Bechgaard salt is the existence of a series of phase transitions induced under a magnetic field. Above a temperature-dependent threshold field a transition from a metallic state into a semimetallic FISDW state is found. A cascade of first-order transitions to successive FISDW subphases exhibiting the QHE has given rise to a complex temperature-magnetic field phase diagram.[1,2] In high field ($H >$ 18–20 T) a semiconducting n=0 SDW state is observed. There is an excellent agreement with the quantized nesting model.[7]

Despite the high degree of the quantization experimentally observed in the Hall effect, an enigmatic behavior in the magnetoresistance is observed. In addition to the anomalously large magnetoresistance in the metallic state, a sharp increase in the magnetoresistance is brought about due to the FISDW transitions. The magnetoresistance typically increases by better than five orders of magnitude between zero field and 20 T. Although the magnetoresistance is somewhat reminiscent of the conventional QHE, a nonvanishing magnetoresistance suggests dissipation yet unaccounted for. As a measure of the "entropy" per carrier, thermopower can discern whether or not a heat current accompanies the electric current in the FISDW transport. As a collective QHE-like system, a vanishing thermopower is expected for the FISDW states in the quantum Hall regime as in conventional QHE samples.[8] On the other hand, a diverging thermopower, typical of semiconductors, is expected for the insulating n=0 state.

The entire range of FISDW transitions in $(TMTSF)_2PF_6$ has been covered in our experiment. A finite but small thermopower is observed in the metallic state. The thermopower increases sharply at the FISDW threshold field. The thermopower is vanishingly small in the QHE regime, consistent with the FISDW being a QHE system. The temperature dependence of magnetoresistance, Hall effect, and both longitudinal and transverse thermopower (Nernst effect) suggests that the FISDW is an unusual type of QHE, distinguished by a temperature-dependent gap. Most surprisingly, the thermopower in the insulating $n=0$ state is also found to vanish at low temperature, perhaps as a consequence of edge states in the open-orbit direction in the Bechgaard salts.

The experiment was performed using a miniature pressure clamp which was immersed in the ^3He space of the cryostat. The details of the pressure cell are described elsewhere.[2] The experiment at Princeton University was done using a superconducting solenoid, and a Bitter magnet was used at the National Magnet Laboratory. A technique prescribed for thermoelectric power measurements under pressure[9] was utilized. Because of the loss of sensitivity of thermocouple wires at low temperature, two thin-film resistors were attached to the ends of the sample and used as thermometers to measure the temperature difference. Due to the size restriction from the pressure cell, the typical sample size used was 1.5 x 0.2 x 0.2 mm.[3] Gold wires were used to make electrical contacts in a six-probe configuration, allowing for simultaneous measurement of magnetoresistance, Hall effect, longitudinal thermopower, and transverse thermopower. The contribution of the gold wire leads to the total thermopower was negligibly small. The temperature gradient across the sample was less then 50 mK at low temperature.

In Fig. 1 we present the magnetoresistance ρ_{xx}, the Hall effect ρ_{xy}, the longitudinal thermopower S_{xx}, and the transverse thermopower S_{xy} of a $(TMTSF)_2PF_6$ sample under 11 kbar of pressure at 0.5 K. The transition into the FISDW state is observed at 6.5 T as a cusp in the magnetoresistance and an upturn in the Hall effect. A series of eight transitions is found with clean, quantized Hall plateaus at the lower n values. Above 20 T a transition into the $n=0$ state is found where ρ_{xx} increases by two orders of magnitude and where ρ_{xy} is not well defined. The series of transitions is readily observed in thermopower as well. S_{xx} and S_{xy} are small in the metallic state below the threshold field. At the threshold field the thermopower turns over abruptly, qualitatively following the change in the Hall effect and the magnetoresistance. Slightly above 11 T (near the transition into the $n=3$ FISDW state) both S_{xx} and S_{xy} begin to turn toward zero. High-field transitions ($H > 10$ T) are more apparent in S_{xy} than in S_{xx}, as the S_{xy} decreases in an almost steplike fashion. A peak in thermopower at 15.5 T, corresponding to the transition to the $n=1$ state, is observed. Most surprisingly, despite the dramatic change in resistance at the transition from the $n=1$ to the $n=0$ state, there is virtually no change in thermopower in either longitudinal or transverse directions. Instead of a divergent thermopower typical of semiconducting systems, we observe a small thermopower in the $n=0$ state. This behavior is also observed in temperature sweeps at fixed magnetic field.

In Fig. 2, the temperature sweep of ρ_{xx} and ρ_{xy} of a $(TMTSF)_2PF_6$ sample under 10.5 kbar for the $n=0$, 1, 2, and 3 FISDW states is presented. The Hall resistance is very small in the metallic state below the FISDW transition temperature and then increases precipitously, reflecting the decrease in the number of conduction electrons due to the SDW distortion. Saturation in ρ_{xy} occurs for the $n=1$ and 2 states below 1 K. The magnetoresistance also increases near the onset of the transition and then turns over toward zero near the temperatures where ρ_{xy} begins to saturate. In the insulating $n=0$ state, ρ_{xx} continues to increase as it approaches low temperature. An accurate determination of the Hall effect in the $n=0$ state was not possible due to the high longitudinal resistance.

In Fig. 3, the results of fixed field temperature sweeps of S_{xx} and S_{xy} are presented. The temperature dependence for the different FISDW subphases is very similar to the behavior of ρ_{xx}. The thermopower abruptly increases at the transition temperature and then decreases more rapidly than linear in temperature when ρ_{xy} begins to saturate. Similar behavior is also observed in the insulating $n=0$ state. With decreasing temperature the thermopower increases and then decreases toward zero even though the resistance is increasing monotonically. One interesting feature of the temperature sweep results is that the thermopower of the various FISDW subphases tends to zero at different rates, so a constant temperature, magnetic-field sweep results in the "steplike" be-

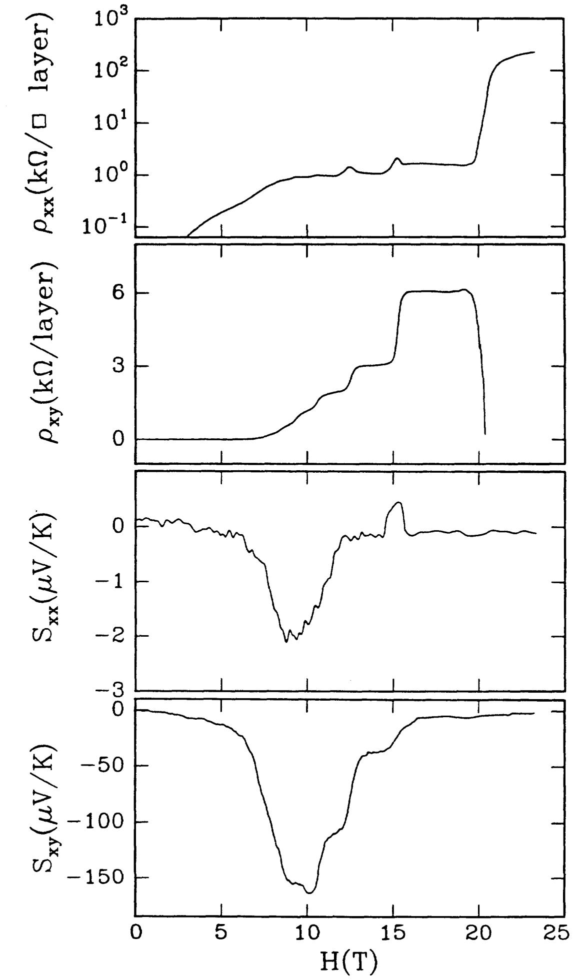

FIG. 1. Magnetotransport and magnetothermopower measurements of $(TMTSF)_2PF_6$ under 11 kbar of pressure and at 0.5 K.

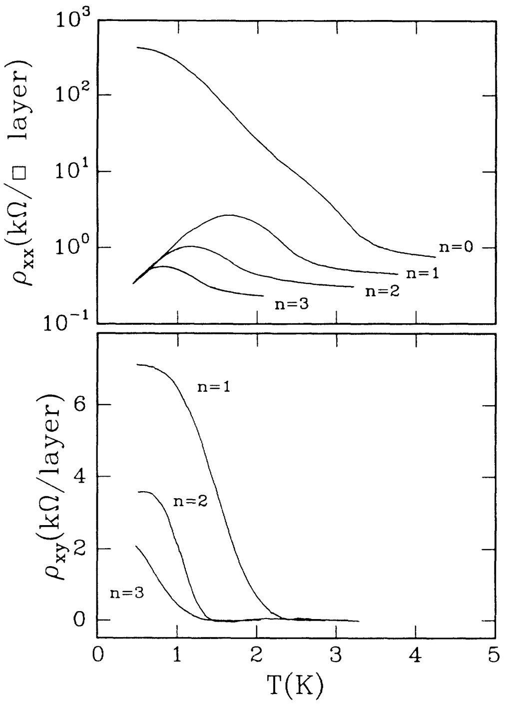

FIG. 2. Temperature sweep of magnetoresistance and Hall effect of (TMTSF)$_2$PF$_6$ sample under 10.5 kbar of pressure at 22.7, 16.8, 13.3, and 11 T for the n=0, 1, 2, and 3 states, respectively.

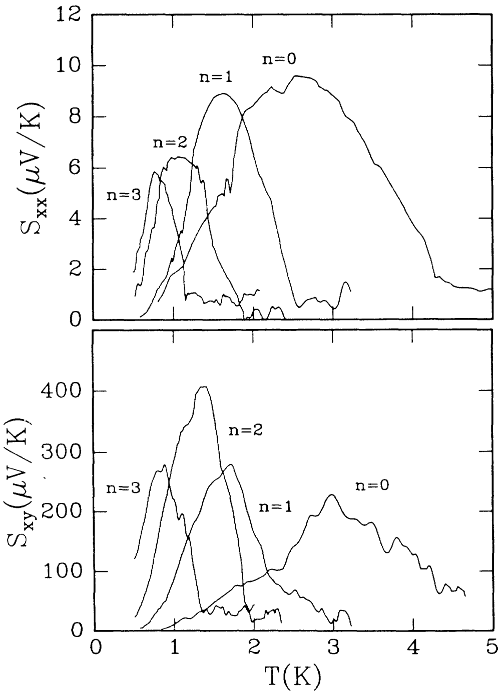

FIG. 3. Temperature sweep of the longitudinal thermopower S_{xx} and the Nernst effect S_{xy} under 10.5 kbar of pressure at the same magnetic fields as in Fig. 2.

havior observed in Fig. 1.

The interesting temperature dependence observed in both resistance and thermopower distinguishes the FISDW states from the conventional QHE. In the conventional QHE a zero thermopower and an activated behavior in conductivity is observed. In the case of FISDW the thermopower initially increases below the transition temperature and then quickly approaches zero typically below half the FISDW transition temperature. A similar increase below the transition temperature, followed by a decreasing behavior in the magnetoresistance, suggests that the conductivity is also activated in the FISDW states. The observed, nonzero magnetoresistance may be a finite-temperature effect. Thus, the activated behavior in conductivity and vanishing thermopower seems to be a universal behavior of all QHE systems, either conventional or unconventional.

The unusual temperature dependence suggests the presence of a gap in the spectrum; instead of the usual Landau gap in the conventional QHE, the gap in this case is a SDW gap arising due to many-body interactions.[3] Within the framework of the "standard model," the cascade of FISDW transitions and QHE comes about from the proximity of the SDW at low pressures and the deviation from perfect nesting.[7] Application of a magnetic field, which energetically allows for a partial (imperfect) nesting of the Fermi surface and the subsequent Landau quantization of the remaining pocket of carriers, leads to the formation of the FISDW. The resulting semimetal, with an energy spectrum of a series of bands and gaps, lowers the energy by always pinning E_f in one of the gaps. Thus, by Laughlin's gauge-invariance argument,[10] an integrally quantized Hall effect and a behavior akin to the conventional QHE are expected.

In order to see what is consistent with our understanding of the FISDW states and what is unusual, we have modeled the transport in terms of QHE-like conduction from the filled Landau bands plus transport from excitations over the SDW gap. In the presence of an electric field $\mathbf{E}$ and temperature gradient ∇T, the electric current is given by $\mathbf{j} = L^{11}\mathbf{E} + L^{12}\nabla T$, where L^{11} and L^{12} are transport coefficient tensors. The conductivity and thermopower are related to the transport coefficients L^{11} and L^{12} by[11]

$$\sigma_{ij} = L^{11}_{ij}, \qquad \rho_{ij} = (L^{11})^{-1}_{ij}, \tag{1}$$

$$S_{ij} = (L^{11})^{-1}_{ik} L^{12}_{kj}. \tag{2}$$

The L^{11} tensor is the conductivity tensor σ as given above. The L^{12} tensor is the thermoelectric tensor given by $L^{12} = \frac{1}{eT}\int d\varepsilon \left(-\frac{\partial f(\varepsilon)}{\partial \varepsilon}\right)(\varepsilon - \mu)\sigma(\varepsilon)$, where $f(\varepsilon)$ is the Fermi function. In the FISDW states the Fermi level is always between filled and empty Landau bands. We therefore take the conductivity and thermopower tensors for the integer QHE case and add the contributions from the excitations. For the pure integer QHE case the only nonvanishing component of L^{12} and L^{11} is $L^{11}_{xy} = \sigma_{xy} = ne^2/h$. We then have

$$\sigma_{xx} = Ae^{-\Delta(T)/T}, \tag{3}$$

$$\sigma_{yy} = Be^{-\Delta(T)/T}, \tag{4}$$

$$\sigma_{xy} = \frac{ne^2}{h}(1 - e^{-\Delta(T)/T}) + Ce^{-\Delta(T)/T}, \tag{5}$$

$$L^{12}_{xx}, L^{12}_{yy} \sim \left(\frac{\Delta(T)}{2eT}\right) e^{-\Delta(T)/T}, \tag{6}$$

$$L^{12}_{xy} \sim C\left(\frac{\Delta(T)}{2eT}\right) e^{-\Delta(T)/T}, \tag{7}$$

where $\Delta(T) = \Delta_0(1 - T/T_c)^{1/2}$ near the transition temperature T_c and A, B, and C are the normal state σ_{xx}, σ_{yy} and Hall conductance.

In testing the model, a phase diagram similar to that of the experiment was first generated. The gap functions were then chosen to have a BCS-like form with an adjustable prefactor [i.e., not set by $2\Delta(0) = 3.52k_BT_c$]. The conductivity tensor elements are constrained by the condition that the normal state resistivity be recovered in the metallic state. By varying the gap structure, fair agreement with the experiment can be reproduced. The results are shown in Fig. 4. Comparing this figure with the experiments we see that for $n > 0$ the only qualitative difference is that the longitudinal resistance decreases much less rapidly than expected. This would tend to indicate the presence of some parallel conductance (at least in σ_{yy}) which is increasing with decreasing temperature.

The other major difference is in the behavior of the n=0 state. It should have a diverging resistance and thermopower as temperature is lowered reflecting the insulating behavior expected. The resistance increases and then levels off at a value about three orders of magnitude higher than the normal metallic state while the thermopower looks surprisingly like the $n > 0$ states. It is the vanishing thermopower in a supposedly insulating phase which is the most unexpected feature. Even though it is theoretically possible to coincidently have zero thermopower in a semiconductor from exact electron-hole symmetry, in virtually all semiconductors the thermopower is large and temperature dependent and usually strongly sample dependent. The vanishing thermopower in the n=0 state has been observed on all three samples we have measured under pressure.

Since the temperature dependence of the thermopower in the n=0 state is identical to the other FISDW subphases, it is tempting to ascribe the behavior in the n=0 state as a consequence of a collective nature of the state as in the other subphases. In such a case, some novel type of collective *excitation*, instead of QHE-like behavior, may be responsible for the vanishing thermopower for the n=0 state.

The vanishing thermopower in the n=0 state may also be a consequence of a parallel channel of conduction perhaps due to the open-orbit edge states.[12] A system consisting of FISDW transport in the bulk and a shorting parallel resistor, that exhibits metallic properties (including a small, finite thermopower), can result in a large but finite magnetoresistance and a vanishing thermopower in the n=0 state at low temperature. Unlike bulk states, edge states do not participate in SDW transitions since the states with which they would pair are outside the sample. States within a magnetic length $(4t_b/\hbar\omega_c)b$ from the edge (parallel to the chain direction) do not undergo FISDW transitions. For a typical sample, the edge states would consist of roughly one-thousandth of the sample at 20 T. The resistance jump at the n=0 transition of two to four orders of magnitude and the weakly magnetic-field-dependent resistance at higher field suggest such a small metallic parallel short.

For a system with two parallel components of resistance and thermopower, the resulting conductivity and thermopower is simply

$$\sigma_{\text{total}} = \sigma_{\text{edge}} + \sigma_{\text{FISDW}}, \tag{8}$$

$$S_{\text{total}} = \frac{\sigma_{\text{edge}}S_{\text{edge}} + \sigma_{\text{FISDW}}S_{\text{FISDW}}}{\sigma_{\text{total}}}, \tag{9}$$

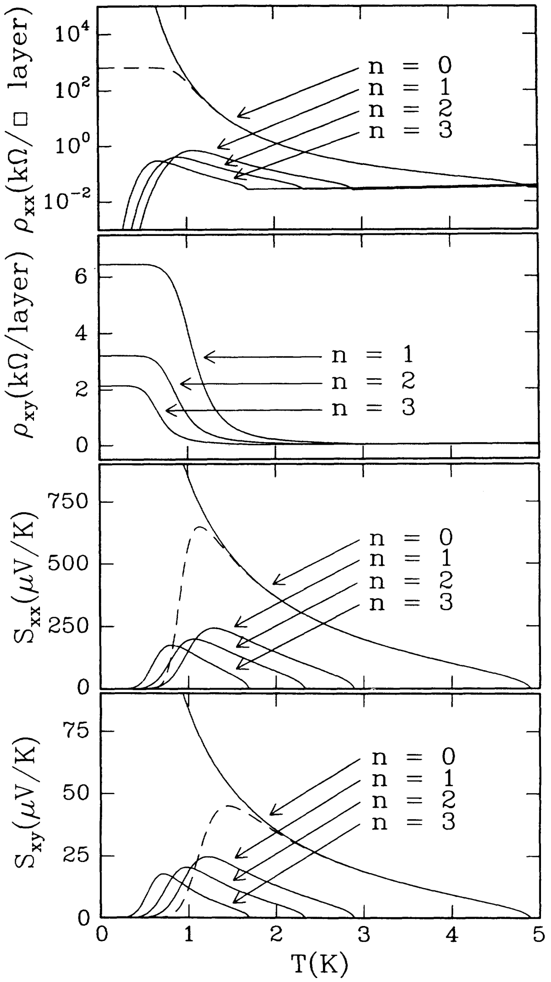

FIG. 4. Calculated transport properties (from top down, longitudinal and Hall resistance, thermopower and Nernst coefficient) from the model presented in Eq. (7) for a BCS-like gap with zero-temperature values 8.5, 6.1, 4.3, and 3.2 K for the n=0, 1, 2, and 3 states, respectively. The dashed curves are for the parallel short (edge state) model given by Eq. (9).

where $\sigma_{\text{edge}}(\sigma_{\text{FISDW}})$ and $S_{\text{edge}}(S_{\text{FISDW}})$ are conductivity and thermopower contributions from the edge (FISDW) channel of conduction. Since the size of the edge state orbit varies inversely with magnetic field, we have modeled the edge states' magnetoresistance as $\rho_{\text{edge}}(H,T) = \rho_0 + aHT$, where a is a constant. In Fig. 4 the dashed curves show the calculated behavior for the $n=0$ state in the presence of a parallel resistance along the x direction (as distinct from a parallel bulk conductance along x). The parallel resistance has virtually no effect on the $n \neq 0$ states.

Another interesting feature of the data which is not reproduced in the transport model given in Eqs. (3)-(7) is that S_{xy} is larger than S_{xx} by at least a factor of 50. This is surprising since the ratio of S_{xy}/S_{xx} is even larger than ratio $\rho_{xy}/\rho_{xx}{=}\tan\Theta_H$, where Θ_H is the Hall angle. One simple explanation may be that the thermopower is much less sensitive to crystal imperfections and geometry than resistance. Thus, the conductivity Hall angle may be less reliable. Another possibility is a parallel metallic edge short which reduces the measured voltage along the x direction of the sample but not along the y direction.

The persistence of this behavior in a variety of samples leads us to the conclusion that the vanishing thermopower is an intrinsic property of the $n=0$ state. The anomalous vanishing thermopower, combined with the insulating behavior in resistance, sets the $n=0$ state apart from other FISDW states. The other FISDW subphases in $(\text{TMTSF})_2\text{PF}_6$ are semimetallic and the low-temperature thermopower vanishes due to the QHE.

Recently, a thermoelectric power experiment was reported on a related salt $(\text{TMTSF})_2\text{ClO}_4$.[13] A strong deviation from the standard model predictions is observed in the ClO_4 salt. Instead of an $n=0$ state after $n=1$, there exists a semimetallic state that displays a reentrant behavior in the phase diagram,[14] followed by a newly identified semiconducting phase.[13] Based upon Hall effect measurements, a possible "$n = \frac{1}{3}$" fractional QHE has been proposed for the reentrant semimetallic state.[15] A vanishing thermopower is observed in this "$n = \frac{1}{3}$" state, consistent with the collective nature of the state. Furthermore, a divergent thermopower in the semiconducting phase above 27 T allowed for the identification of the new phase with an energy gap.

It has been speculated that this semiconducting phase is a candidate for the missing $n=0$ state in ClO_4.[16,17] However, the low-temperature thermopower in the $n=0$ state in $(\text{TMTSF})_2\text{PF}_6$ and the high-field phase in $(\text{TMTSF})_2\text{ClO}_4$ are very different even though both phases are semiconducting: divergent in the ClO_4 insulating state and vanishing in the PF_6 $n=0$ state. Thus, the dissimilar thermopower between the two semiconducting phases is the strongest argument that the high-field phase in $(\text{TMTSF})_2\text{ClO}_4$ may not be the $n=0$ state and may be categorically different from the other FISDW states.

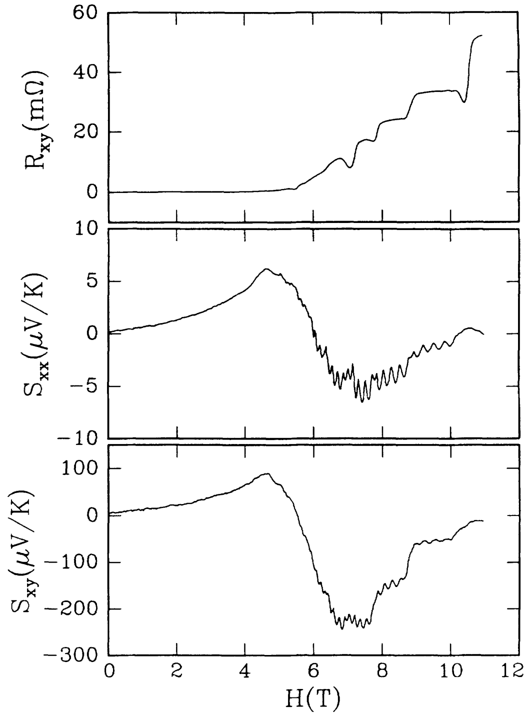

FIG. 5. Hall effect, longitudinal thermopower, and transverse thermopower under 8.5 kbar of pressure at 0.5 K.

In Fig. 5 the Hall effect and thermopower measurements of another sample at 8.5 kbar is presented. The qualitative feature of the data is similar to that of Fig. 1. The most interesting feature of the data is the presence of so-called "rapid" oscillations in thermopower. These magneto-oscillations are typically observed for all magnetic-field ranges in other Bechgaard salts. The oscillations in $(\text{TMTSF})_2\text{PF}_6$ have been of some interest due to their detection only in the $n=0$ state. Our thermopower results show that the "rapid" oscillations also exist below the $n=0$ state. Similarly pronounced oscillations have been previously observed in thermopower measurements in $(\text{TMTSF})_2\text{ClO}_4$.[13]

In summary, we have performed magnetothermopower measurements on $(\text{TMTSF})_2\text{PF}_6$. Zero thermopower in the FISDW states suggests collective, QHE-like transport. Most surprisingly, we observe an unexpected property of the semiconducting $n=0$ state: the vanishing of its thermopower at moderate temperatures. We suggest one possible explanation in terms of open-orbit edge states. Finally, rapid oscillations are also observed below the $n=0$ state in $(\text{TMTSF})_2\text{PF}_6$.

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