Spin-Density-Wave Transitions in a Magnetic Field

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(Received 7 October 1985)

We report new Hall measurements on $(TMTSF)_2PF_6$ under pressure. Our data, and a simple model, directly link the novel magnetic-field–induced state first seen in the Bechgaard salts to a well-characterized ambient-pressure spin-density-wave state. Comparison of the data for different salts suggests that (1) incommensurability associated with a two-dimensional lattice in a magnetic field splits the Landau levels into Landau subbands, and (2) coupling to soft modes changes the field-induced spin-density-wave transitions from second order to first order.

The unusual behavior in high magnetic fields and at low temperatures of the Bechgaard salts,[1] $(TMTSF)_2X$ (TMTSF is tetramethyltetraselenafulvalene and X is PF_6, ClO_4, etc.), is one of the most interesting current problems in the area of organic conductors. In the original observations, on the PF_6 salt under pressures sufficient to suppress the ambient-pressure semiconducting spin-density-wave (SDW) ground state, Shubnikov–de Haas–type oscillations of the magnetoresistance appeared above a sharp temperature-dependent threshold field.[2],[3] This result is remarkable because there are no closed orbits on the quasi two-dimensional Fermi surface common to these materials. Several authors argued that under pressure the SDW exhibits a semimetallic regime (hence the oscillations),[4],[5] and nuclear magnetic resonance experiments implied that the high-pressure, high-field (or field-induced) state is magnetically ordered.[6] But there has been no evidence directly linking the SDW and field-induced states.

In this paper we report magnetotransport studies on $(TMTSF)_2PF_6$ under pressure which link the ambient-pressure SDW and high-pressure, high-field states. Specifically, the SDW transition temperature near 6 kbar shows an enhancement in magnetic field that is orbitally driven, and a simple semiempirical formula for the transition temperature of a two-dimensional system under pressure and magnetic field fits both the SDW enhancement and the transition (threshold) to the high-field state near 7 kbar. We also report steplike structure and sudden sign reversals in the Hall effect at 7 kbar, similar to the behavior of $(TMTSF)_2ClO_4$ at ambient pressure. The sign reversals are reminiscent of the predictions of Thouless.[7] Finally, we suggest that the physics in $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ is essentially the same, and that persistent differences in the behaviors of the two salts may be due to coupling to soft vibrational modes associated with the anion-ordering transition in the latter.

The threshold and oscillations also appear in $(TMTSF)_2ClO_4$ at zero pressure—in the magnetoresistance,[2],[8] Hall effect,[9],[10] and magnetization.[11] The Hall measurements imply a steplike decrease in effective carrier density at each oscillation along with plateaus reminiscent of the quantum Hall effect.[12] The Hall data of Ref. 10 show anomalous sign changes between some of the steps. The magnetization results imply that the oscillations are actually a series of first-order phase transitions.

Some aspects of the behavior of the PF_6 and ClO_4 salts are significantly different. In the latter, the threshold and oscillation positions are temperature dependent and magnetically hysteretic, and the oscillations are only poorly periodic with inverse field. These differences have posed a problem for models suggesting a common physical mechanism for the field-induced state in these materials.

Recent theoretical work has shown that a two-dimensional open-orbit metal is unstable in the presence of a magnetic field normal to the plane, because of the quasi one-dimensional character of the electronic motion.[13-17] The actual situation is complicated by the spatial incommensurability of the periodicities imposed by the lattice, the spin-density wave, and a magnetic field.[14] For a square lattice in a magnetic field, Hofstadter found that the Landau levels split into subbands whose number depends on the closest rational representation to the density of flux quanta per unit cell.[18] Thouless found that these subbands can cause anomalous sign changes in the Hall effect.[7] The present situation is distinguished from the hypothetical model of Hofstadter by the presence of anisotropy and the SDW, but the energy spectrum should still contain complex subbands caused by the interplay of incommensurate potentials.

Data between 1.04 and 4.02 K were taken with simi-

lar results on six crystals grown both at Argonne National Laboratory and at Exxon. The samples were mounted on 25-μm gold wires by use of gold or silver paint; six evaporated-gold contacts were applied to each crystal: two on the ends for current along the highly conducting a or [100] axis, and two pairs arranged on the (001) face to serve as voltage probes for both magnetoresistance and Hall effect. The applied magnetic field of up to 107 kOe was completely rotatable in the plane normal to a. The data were taken with field oriented along the c^* direction normal to both a and b, except where noted otherwise. The Hall resistance was obtained from the difference in voltage between two field sweeps with field rotated by 180° ±0.2°. The samples were pressurized in helium gas with an accuracy of 0.2 kbar and a resolution of 0.05 kbar. Although the SDW transition decreases rapidly with pressure near 6 kbar, the fine control possible with the solid-helium pressure-generation technique enabled us consistently to achieve zero-field SDW transition temperatures near 2 K.

Figure 1 illustrates typical Hall behavior at the metal-SDW phase boundary near 6 kbar. Note first the Hall resistance in low fields for a typical sample at 4.0 K, in the metallic regime, and at 2.1 K, just below the zero-field SDW transition temperature of 2.2 K. The Hall effect is small and negative in the metallic state, but positive and much larger in the SDW state. The change in sign is presumably related to details of the Fermi surface and transport. Using the simple free-electron model, we find a carrier density of about
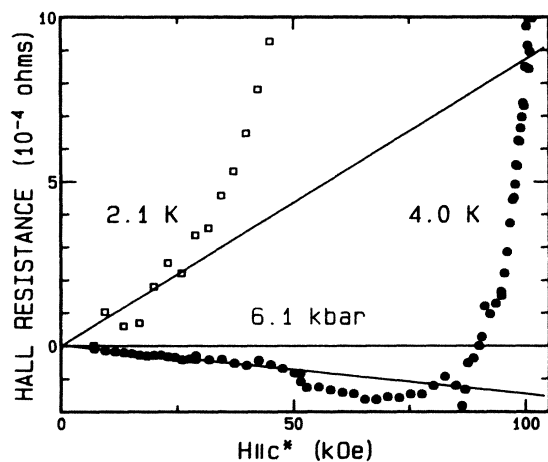
10^{21}/cm^3 in the metallic state [similar to that of (TMTSF)$_2$ClO$_4$ in low fields],[9] and 10^{20}/cm^3 in the SDW state. We will report elsewhere data indicating that the initial transition is to a semimetallic phase, as predicted by Yamaji,[4] with an eventual semiconducting phase at lower temperatures or higher fields.[19] Coleman et al. recently reported a similar effect in the charge-density-wave system NbSe$_3$.[20] Now note the high-field behavior at 4 K: The magnitude and sign change fairly abruptly toward the values observed in low fields at 2.1 K, implying an enhancement of the SDW transition temperature in a field. We also observed the enhanced transition through resistivity versus temperature in constant field,[21] but were able to map out the field dependence of the enhancement more accurately from the Hall resistance versus field at different temperatures.

The phase diagram of Fig. 2(a) summarizes our data on the SDW enhancement for a typical crystal near 6 kbar. Note that the SDW transition temperature increases nearly quadratically as a function of field. The magnitude of the enhancement is similar to those of the transitions from metal to high-field state in the present compound near 7 kbar [Fig. 2(b)] and in (TMTSF)$_2$ClO$_4$ at ambient pressure.

The dependence of the enhancement on field orientation provides vital information. We find that only the c^* component of field is relevant, exactly as for the threshold to the high-field state.[2] This observation proves that the SDW enhancement, like the threshold, is due to orbital rather than spin effects, since the c^* direction is not the easy axis for spin alignment,[22] but is the normal to the highly conducting a-b plane.
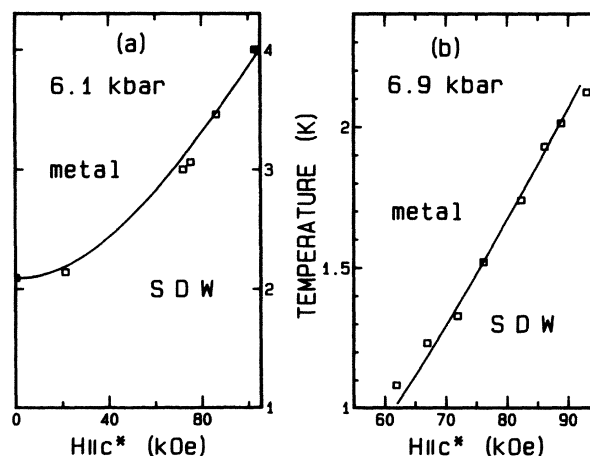
Our observations thus establish a clear link between

FIG. 1. Typical (TMTSF)$_2$PF$_6$ behavior at the metal-SDW phase boundary near 6 kbar: Hall effect vs field at temperatures above (4 K) and below (2.1 K) the SDW transition. Note the differences in both sign and magnitude at low fields: At 4 K the sample is metallic, but at 2.1 K it is a SDW semimetal. The scatter in the data at 2.1 K is due to a large background subtraction. The high-field data at 4 K show the onset of the field-enhanced SDW transition.

FIG. 2. (a) Typical (TMTSF)$_2$PF$_6$ temperature-field phase diagram near 6 kbar (see text). The curve represents a fit of Eq. (2) to the metal-SDW phase boundary. (b) Fit of Eq. (2) to the threshold field at 6.9 kbar (data from Refs. 2 and 3). The same parameters as in (a) are used.

the ambient-pressure SDW and high-pressure field-induced states, and suggest that both are manifestations of the same phase boundary. We now confirm the link by developing in outline a semiempirical formula to describe the effects of both pressure and magnetic field on the SDW transition, and showing that it also fits the threshold to the field-induced state near 7 kbar. A more comprehensive treatment of the model will be presented elsewhere.[23]

Consider first the situation of an anisotropic two-dimensional system with no magnetic field. Following Ref. 14, we examine the "joint" density of states, N_j, arising from nesting of the Fermi surface by a SDW with effective strength V. The transition temperature is then given by the BSC-type relation $T_c = T_0 \exp(-1/N_j V)$, where T_0 is a measure of the electron-electron coupling. The degree of nesting, and hence N_j, depend on the ratio of the associated energy gap (or order parameter) Δ to the transverse bandwidth t_b: $N_j \approx N_0 \Delta / 2t_b$ to first order in Δ, where N_0 is the one-electron density of states. Gor'kov[13]

uses an effective unnested transverse bandwidth, t_b', in place of t_b. Assuming that pressure increases t_b or decreases V until there is no transition above some pressure P_0, we let $N_j V = D(1 - P/P_0)$ with D constant. Then we have

$$T_c(P) = T_0 \exp[-1/D(1 - P/P_0)] \qquad (1)$$

for the transition in zero field. Note that the expression is meaningful only for $P < P_0$. Equation (1) provides a good fit to the pressure data on the PF_6 salt[24] with $T_0 = 16$ K, $D = 3.4$, and $P_0 = 7.2$ kbar.

A magnetic field enhances the SDW nesting by condensing the transverse momentum states into a one-dimensional band of width $\hbar \omega_c$, where ω_c is the effective cyclotron frequency $eHk_F b/mc$. N_j now includes all states nested by $2k_F \pm \omega_c/v_F$, where v_F is the Fermi velocity. The electronic dispersion is no longer free-electron-like as in Ref. 14, because of the gap Δ. We find, using a nearly-free-electron dispersion, that $N_j \approx (N_0/2t_b)[\Delta^2 + (\hbar \omega_c)^2]^{1/2}$. Introducing pressure as we did for Eq. (1), we finally obtain

$$T_c(P,H) = T_0 \exp(-1/\{(AH)^2 + [D(1 - P/P_0)]^2\}^{1/2}), \qquad (2)$$

where A is a constant. Using the parameter values above, and the 6.1-kbar data at 100 kOe from Fig. 2(a), we find that $A = 5 \times 10^{-3}$ kOe^{-1}. ($P = 6.2$ kbar, used in the fit so as to match the measured zero-field T_c, is equal to the experimental pressure of 6.1 kbar within our experimental accuracy.)

There is striking agreement between Eq. (2) and the data over a broad range of pressure and field: The fit to the quadratic behavior for intermediate fields at 6.1 kbar is indicated by the curve in Fig. 2(a). Moreover, at $P = 0$, Eq. (2) predicts a mere 0.05-K increase in T_c at 100 kOe; this is entirely consistent with ambient-pressure measurements that found no field dependence, within their accuracy.[25,26] Finally, Eq. (2), with all the same parameter values as above, provides a good fit to the metal–high-field-state phase boundary at 6.9 kbar, as shown by the solid curve in Fig. 2(b).[27] This result confirms our conclusion that the field-induced state is an extention of the ambient-pressure SDW.

We now discuss measurements taken at 7.0 kbar, where the ground state in zero field is superconducting. Some of these data were reported elsewhere,[21] but only for a single sample and without the current interpretations. The magnetoresistance results are consistent with the early data on $(TMTSF)_2PF_6$ and reaffirm the differences in behavior from $(TMTSF)_2ClO_4$, particularly the absence of hysteresis or temperature dependence in the oscillations.

At low fields the Hall coefficient is small and negative, -0.004 cm^3/C, identical to the 6-kbar metallic-state data. Typical Hall data taken in high fields at

1.07 K are shown in Fig. 3. The similarities to the behavior of $(TMTSF)_2ClO_4$ at ambient pressure are obvious: steplike structure and sharp reversals of sign near 100 kOe. Note that the data are not unambiguously identifiable as plateaus, unlike the case for $(TMTSF)_2ClO_4$.

The dramatic sign reversals near 100 kOe are very

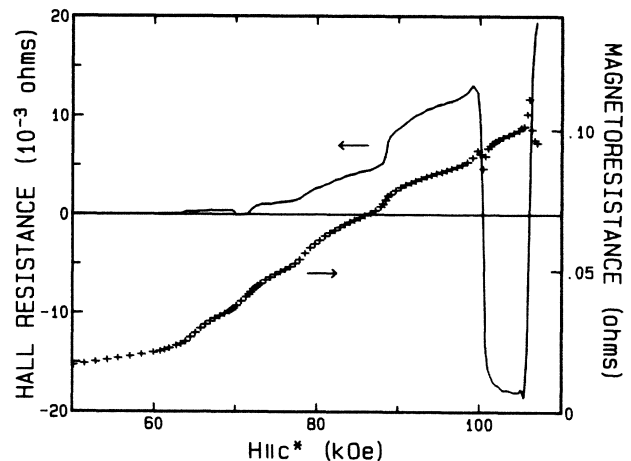FIG. 3. Hall resistance and magnetoresistance vs magnetic field for a typical $(TMTSF)_2PF_6$ crystal at 7.0 kbar and 1.07 K. Note the steplike structure and the anomalous reversals in sign of the Hall effect near 100 kOe. The sharp peaks in the magnetoresistance associated with the Hall sign reversals are due to imperfect subtraction of the Hall voltage.

reminiscent of the theoretical results of Thouless for a two-dimensional metal in a magnetic field. This implies that the energy spectrum is split into subbands as a result of the incommensurability of the field-induced periodicity with that of the lattice (or SDW), *a la* Hofstadter. Heritier *et al.* argue that the similar effect in $(TMTSF)_2ClO_4$ is due to a complicated Fermi surface generated by anion ordering.[16] The PF_6^- anion, however, presumably because of its closer approximation to spherical symmetry, does not exhibit such ordering.

The Hall behavior, while suggesting a series of quantized steps, is not consistent with a simple quantum Hall effect.[21] A similar finding in $(TMTSF)_2ClO_4$ prompted the proposals of a series of phase transitions reducing carrier number.[8,9] However, the discrepancies in behavior between the PF_6 and ClO_4 salts are not accounted for in any of the current models. We believe that these discrepancies are due to the anion ordering in $(TMTSF)_2ClO_4$. The low temperature at which the ordering occurs, 24 K, implies the presence of very soft vibrational modes. Such soft modes could interact with the electronic states to alter the field-induced transitions from second order to first order, thus introducing the discrepancies noted above.

In summary, we have presented Hall-effect data and a semiempirical formula [Eq. (2)] linking the ambient-pressure and field-induced states in $(TMTSF)_2PF_6$, clearly identifying the latter as an extension of the ambient-pressure SDW phase. An anomalous sign change in the Hall effect at 7 kbar suggests that the incommensurability of the periodicities imposed by the SDW, the lattice, and a magnetic field plays an important role in the transport properties. Our results imply that the high-field states in both $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ arise from native electron-electron interactions as discussed by Horovitz, Gutfreund, and Weger.[5] We suggest that first-order transitions and related distinct behavior seen in the ClO_4 salt may be due to soft vibrational modes associated with the anion-ordering transition in that material.

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[27]Equation (2) does not fit the NMR data of Ref. 3 at 7.6 and 8.3 kbar. Those data are not consistent, however, with preliminary transport data. Also, the interpretation or validity of Eq. (2) above $P_0 = 7.2$ kbar is not clear.