Quantized Hall Effect and a New Field-Induced Phase Transition in the Organic Superconductor $(TMTSF)_2PF_6$

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We report a Hall-effect and magnetoresistance study of single crystals of the organic superconductor tetramethyl-tetraselenafulvalinium hexafluorophosphate, $(TMTSF)_2PF_6$, under hydrostatic pressure at temperatures down to 0.5 K in magnetic fields up to 25 T. There is clear evidence for a quantized Hall effect, with plateaus labeled by the integers $n=5$ to 1, up to 17 T. A new field-induced phase transition to a very resistive state occurs at 18 T. We believe that this is the "$n=0$" spin-density-wave state predicted by the quantized nesting theory.

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Linear-chain organic conductors of the tetramethyltetraselenafulvalinium $(TMTSF)_2X$ family, where X is a monovalent anion, display many interesting properties such as spin-density waves (SDW's), anion ordering, superconductivity,[1] and field-induced spin-density-wave (FISDW) transitions. The latter occur above a threshold field which is typically 6 T at 1 K.[2]

As explained in Refs. 3 and 4 the basic physical reason for the FISDW transitions is that application of a magnetic field along the low-conducting c^* direction makes the electronic motion along the conducting chains more one dimensional and thus restores the logarithmic divergence of the Q-dependent susceptibility,[5] leading to a phase transition.

However, the observation of rather well-defined plateaus[6] in the Hall voltage of $(TMTSF)_2ClO_4$ at values reasonably close to $h/2ne^2$ per molecular layer, where n is a small integer, gave rise to the idea that a type of quantum Hall effect (QHE) resulting from quantization of nesting[5,7,8] occurs in the FISDW phases, although this is not the only possible interpretation.[9]

In a simple picture the Q vector of the SDW changes with H in such a way as to keep the Landau levels associated with the un-nested electron or hole pockets completely filled over an extended field range. This minimizes the diamagnetic energy at the expense of a slightly worse nesting and gives extended regions where the Hall voltage is quantized.

More precisely[10] the electronic states are determined by the combined effect of two periodicities, the spin-density-wave vector Q and the reciprocal of the magnetic length $\lambda_H = h/beH$, where b is the transverse lattice parameter in the intermediate-conductivity direction. The electronic spectrum of the FISDW phases has a series of gaps located at quantized values of the SDW vector Q, whose component along the chains is given by $Q_\parallel = 2k_F + 2\pi n/\lambda_H$, where n is an integer and k_F is the Fermi wave vector. Thus within a given FISDW phase, $Q_\parallel$ of the SDW increases linearly with H in order to keep the Fermi level within a gap, and then suddenly jumps back to the value corresponding to $n-1$. There is a series of first-order transitions between FISDW phases each with quantized Hall voltage and each labeled by successive integers n.

Recently the ClO_4 salt has been studied[11,12] in magnetic fields of up to 30 T and a second-order transition back to the original metallic state has been identified.[12,13] These results could not be understood within the picture mentioned above. Instead, the Hall voltage was constant over a wide region between 8 and 25 T (it was claimed[11] that it corresponded to fractional quantization) and the $n=0$ phase was not observed. One possible complication regarding the ClO_4 salt is that it has a superlattice associated with anion ordering at 24 K.[1] In principle, measurements on the PF_6 salt, which has no such superlattice, may be easier to interpret, although they are technically more difficult. Similar experiments have recently been performed by another group.[14]

In this Letter, we report Hall-effect and magnetoresistance measurements down to 0.5 K and at fields of up to 25 T under an applied pressure of 8 kbar at low temperatures, which is sufficient to stabilize the superconducting state.

Results for two single crystals are reported here, although magnetoresistance has been measured for several other crystals. The first, of dimensions $3.8\times0.175\times0.25$ mm^3, was measured up to 12 T using a superconducting solenoid at Orsay. The second, $4\times0.25\times0.2$ mm^3, was measured up to 25 T using the hybrid magnet at the Service National des Champs Intenses, Grenoble. On each long side of a crystal, two gold areas (1.1 mm apart and 0.2 mm long) were made by evaporation using a masking technique suggested by L. Forró, giving two pairs of Hall and two pairs of magnetoresistance contacts. Uniform current contacts were achieved by evaporating gold on all sides and over the ends of the crystal. A special tech-

nique was used to attach gold wires to these pads and all contact resistances were less than the measuring limit of 5 Ω even after one month under pressure at room temperature in the isopentane pressure medium. A pressure of 11 kbar was applied at room temperature using a standard BeCu clamp and Teflon cell technique. The pressure clamp was immersed in the ^{3}He space of a homemade high-capacity ^{3}He cryostat. Temperatures were measured with a calibrated germanium thermometer in zero field and with a capacitance thermometer (above 1.5 K) or a home-calibrated RuO_2 chip resistor in a magnetic field. Resistance-temperature, $R(T)$, curves were monitored continuously on cooling. No irreversible jumps associated with microcracks occurred—the only detectable anomaly in the $R(T)$ curve was that at 210 K caused by the freezing of the isopentane.

In order to separate possible magnetoresistance signals from the Hall voltage, the field from the hybrid magnet was reversed on successive days. Care was taken to ensure that the data were not influenced by heating effects or other sources of nonlinearity such as sliding SDW's. Measuring currents as low as 2 μA had to be used above 20 T.

Hall-effect data taken in the hybrid magnet are shown in Fig. 1 for two pairs of Hall contacts on the same single crystal. Below 18 T there are clear plateaus whose heights are in the ratio 1:0.52:0.32:0.24 in both cases. The absolute values of the largest plateaus are 11.6 ± 0.5 and 10.2 ± 0.5 kΩ per molecular layer, taking the c lattice parameter to be 13.3 Å [15] and using the measured crystal thickness of 0.2 ± 0.04 mm.

One of the main results of the present work is that not only are the ratios given by successive integers but the magnitude of the largest plateau corresponds rather well to $h/2e^2$ (12.9 kΩ) per layer, the value expected for the QHE in the presence of spin degeneracy.

As the temperature was raised from 0.5 to 2 K the Hall plateaus developed successively larger slopes. Logarithmic plots of these slopes versus inverse temperature give activation energies in the range 1–4 K. For downward field sweeps the slopes were systematically larger, although the gap obtained is still within the above range.

Figure 2 shows corresponding magnetoresistance data. In the region below 18 T where the resistance was small, the results shown are the average values for normal and reversed field. There are well-defined peaks at the fields where the Hall voltage jumps to the next plateau. In the region between peaks (corresponding to the Hall plateaus) ρ_{xx} is constant and corresponds to a resistance which is 150–220 times lower than h/e^2 or 25.8 kΩ/□ per layer. Thus although ρ_{xx} is not strictly zero, as it should be for the QHE, it is only $\frac{1}{75}$ to $\frac{1}{22}$ of ρ_{xy} at the $n=1$ and 5 plateaus, respectively. For current flow (J_x) along the chains the electric field is therefore nearly perpendicular to the current and the absence of power dissipation required for the QHE is nearly attained. Note that because of the anisotropy this is not the case for J_y.

Substantial hysteresis (in parentheses) between upward and downward field sweeps occurred at 18 T (0.5 T), 14 T (0.37 T), 11.5 T (0.32 T), and 7.4 T (0.08 T), but not for the magnetoresistance peaks at 9.4 and 8 T. The hysteresis at 18 T remained large up to 2 K but then rapidly decreased and it was not detected at 2.8 K.

Above 18 T ρ_{xx} increases rapidly by a factor of 10^4, reaching a value of 0.45 Ω cm or 3 MΩ/□ per layer at 23 T and 0.5 K, which is much larger than h/e^2, i.e., much

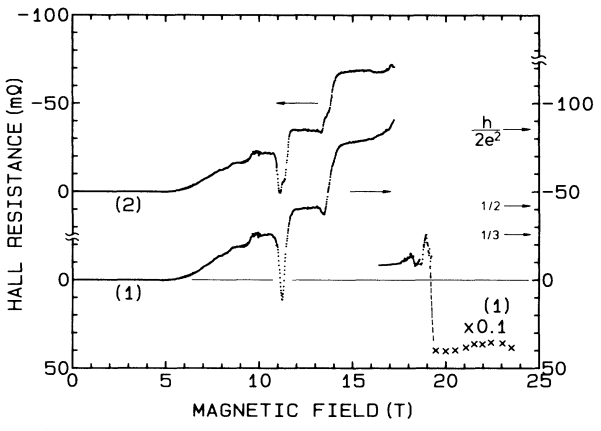

FIG. 1. Hall resistance at 0.5 K vs magnetic field along c^* for two pairs (1),(2) of opposite contacts on the same 0.2-mm-thick $(TMTSF)_2PF_6$ single crystal. The lower right part is the Hall resistance of pair (1) on a reduced scale. The quantized values $h/2ne^2$ (12.9/n kΩ) per molecular layer are marked on the right for contact (1).

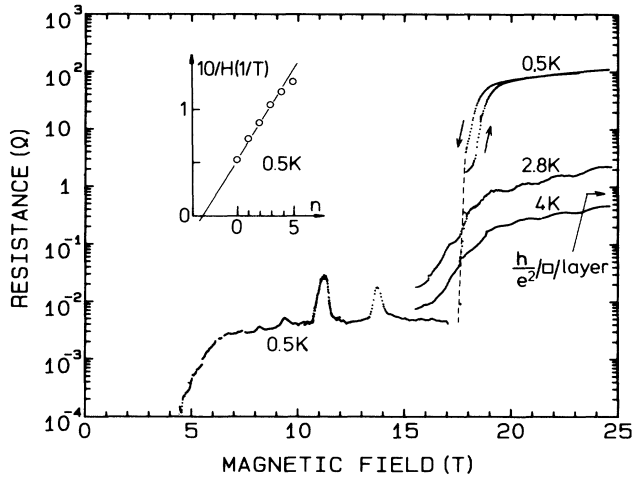

FIG. 2. Logarithmic plots of longitudinal resistance (Ω) vs magnetic field (T) for the same crystal as Fig. 1, at three temperatures. The data have been averaged for forward and reversed field directions. Inset: Midpoints of the jumps in Hall voltage (or the resistance maxima) at 0.5 K as plot of $1/H$ vs successive integers.

larger than the value expected for the fractional quantum Hall effect.[11,16] The Hall effect is negative in the region of the high-field plateaus but changes sign and becomes holelike above 19 T.

Figure 3 shows Hall data for another crystal up to 12 T at a lower temperature (0.36 K). The largest plateau is not attained at 12 T, but the others are in the ratios 0.5:0.32:0.24:0.2 with an absolute value of 14.4 ± 0.8 kΩ per layer expected for $n=1$. For the other pair of contacts a lower value corresponding to 8.6 kΩ per layer was obtained and the plateaus were not as clear. Changes in sign of ρ_{xy} are evident at 10, 7, and 5 T; these rapidly disappear as the temperature is raised. Generally speaking, these sign changes go together with large hysteresis. There is also a tendency for the Hall plateaus to develop fine structure at lower fields and lower temperatures in qualitative agreement with previous investigations.[6] It has been suggested that these features could be connected with the proposed[17] "treelike" splitting of the first-order phase transition lines at very low temperatures arising from higher-order commensurability effects.

The inset to Fig. 3 shows Hall-effect data in the metallic region at 0.5 K below threshold for the same crystal as in Fig. 1. The solid line corresponds to the theoretical expression[9] $R_H = k_F d/Ne \tan(k_F d)$, with $k_F d = \pi/4$, for a quarter-filled hole band, and N corresponding to one hole per unit cell (677 Å^3)[15] which gives $R_H = +3.3 \times 10^{-9}$ m^3/C.

Figure 4 shows the phase diagram obtained from the experimental ρ_{xy} and ρ_{xx} data up to 25 T. The field corresponding to the first-order transition near 18 T is defined by the point of maximum slope on a logρ vs H plot (for H increasing or decreasing) at the various temperatures. As shown in Fig. 4 it is only weakly temperature dependent. The threshold field corresponding to the onset of the FISDW region was determined as the field at which the first anomalous increase in ρ_{xx} appeared. Below 4 K this also corresponded to a large increase in Hall coefficient. Above 4 K an increase in ρ_{xx} was observed without a detectable increase in the Hall coefficient (ρ_{xy} 40 Ω per layer).

As shown in Fig. 2, above 2 K there are oscillations in ρ_{xx} in the high-field phase above 19 T. These oscillations are even more clearly visible in the even part of the Hall voltage, $[\rho_{xy}(H)+\rho_{xy}(-H)]/2$. They are periodic in $1/H$ with a frequency of 286 T. They correspond to the "fast" oscillations[2] observed in various $(TMTSF)_2X$ salts, e.g., $X=PF_6$, ClO_4, and ReO_4, in certain field and temperature ranges and whose origin is not clearly understood. Below 2 K, their amplitude progressively diminishes but, as indicated in Fig. 4, they are still just detectable at 1.0 K.

In the region between 17.6 and 19 T some extra structure was observed in the even part of the Hall voltage; for example, six small peaks at 0.5 K and four at 1.3 K, which are not shown in Fig. 4. The odd part in field (the real Hall signal) did not show this structure.

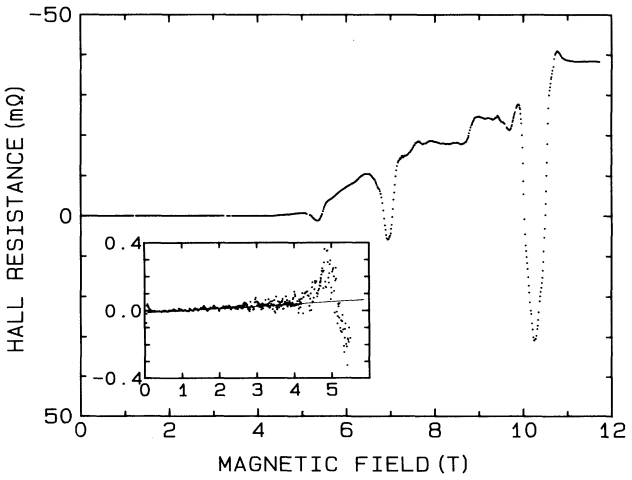

FIG. 3. Hall resistance versus field for a second 0.25-mm-thick crystal of $(TMTSF)_2PF_6$ at 0.36 K again for H parallel to c^*. Note the changes in sign from electronlike plateaus to holelike peaks near 10, 7, and 5 T. Inset: Holelike low-field data and the expected metallic line (see text).

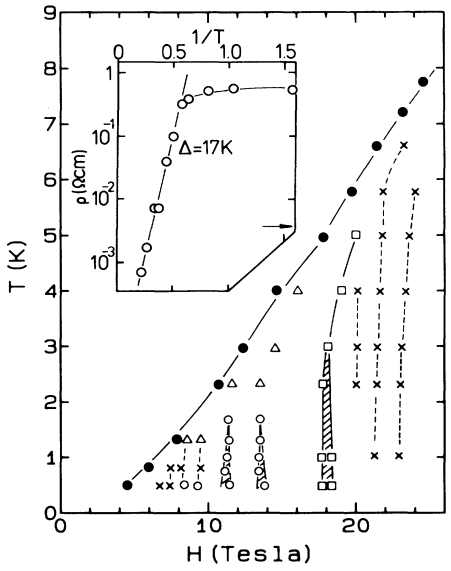

FIG. 4. Phase diagram for $(TMTSF)_2PF_6$ obtained in the present work. Crosses represent peaks in ρ_{xx} and open circles the edges of the Hall plateaus at fixed temperatures. The points taken from maximum slope on logρ_{xx} vs H plots are shown by open squares for the transition to the high-field state and open triangles for others. Filled circles are the threshold fields where there is the first detectable increase in ρ_{xx} or ρ_{xy} (see text). Shaded areas denote hysteresis. Inset: logρ_{xx} vs inverse temperature at a fixed field of 23 T where the arrow denotes a resistivity of h/e^2 per square per molecular layer.

As shown in the inset to Fig. 2, the fields corresponding to the edges of the Hall plateaus follow the law[10] $H=H_f/(n+\gamma)$, with $H_f=60$ T and $\gamma=3.2$. In the quantized nesting theory,[10] H_f is related to the deviations from perfect nesting at zero field; it corresponds to a value $q_{\|}a\simeq 5\times 10^{-2}$, where $q_{\|}$ is the deviation of the longitudinal component of the (zero-field) best nesting vector from $2k_F$, and to a value of t_b' (the characteristic energy associated with imperfect nesting at $H=0$) of the order of 10 K. The latter is consistent with the calculated band structure[18] for a transfer-integral ratio $t_a/t_b \simeq 10$. The above value of γ agrees with the prediction of the nesting model.[10] The physical origin of a nonzero value of γ is that the best nesting vector changes with H and the effective area in $\mathbf{k}$ space becomes smaller at higher fields due to the improved nesting there.

The highly resistive state above 18 T is probably the $n=0$ state predicted in Ref. 10 where at high enough fields there is a large gap at the Fermi energy and the nesting vector is the best zero-field value. As shown in the inset to Fig. 4, at 23 T the resistivity shows thermally activated behavior from above 5 to 1.7 K with an activation energy, 17 K, which is 2.3 times the transition temperature (7.3 K), and this is quite close to the expected BCS value.

We do not understand why the activation plot in Fig. 4 tends to saturate below 1.7 K. It is not an experimental artifact because similar behavior was found in magnetoresistance measurements on two other crystals. In a simple band picture it indicates that a small region of the Fermi surface has a much lower or even zero gap. This would occur if the $n=0$ SDW gap were only just large enough to remove electron or hole pockets (and the energetically unfavorable orbital diamagnetism) at certain points in $\mathbf{k}$ space. However, we have been unable to justify this argument rigorously.

Above 20 T, the Hall coefficient is holelike and it is relatively small for a semiconducting state. Because of the unexpectedly large and temperature-dependent resistivity there, its magnitude is only known to within a factor of 2. To within this accuracy the ρ_{xy} data at 23 T (not shown in the inset to Fig. 4) are parallel to the ρ_{xx} data on a $\log\rho$ vs $1/T$ plot over the whole temperature range (5 to 0.5 K) and also extrapolate to the expected metallic value at 8 K. Such behavior has been observed for several inorganic charge-density-wave systems.[19] It corresponds to a situation where the T dependence of ρ_{xx} is mostly due to changes in the carrier concentration rather than in the mobility.

The main arguments in favor of the $n=0$ state in the PF_6 salt rather than the reentrant metallic state observed in the ClO_4 salt are that (i) as shown in Fig. 4 there is no sign of reentrance in the temperature dependence of the threshold field up to 25 T, (ii) the hysteresis in field at the proposed $n=1$ to 0 transition is similar to that observed for the other transitions, (iii) the transition line at 18 T is only weakly temperature dependent and moves to slightly higher fields above 4 K, and (iv) the onset field corresponds to that expected for the $n=0$ transition, as indicated in the inset to Fig. 2.

However, we have no explanation as to how the fast oscillations can arise in the $n=0$ state.

In conclusion, although some properties mentioned in the text are not fully understood, the main characteristics of the field-induced spin-density-wave phases of $(TMTSF)_2PF_6$ up to 25 T are in excellent agreement with the predictions of the quantized nesting model,[5,10] in contrast to the results for $(TMTSF)_2ClO_4$ in the same field region. Presumably these differences arise from the presence of a superlattice in the latter crystals.

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