Extreme Quantum Limit in a Quasi Two-Dimensional Organic Conductor

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We have measured magnetoresistance, Hall resistance, and magnetization of tetramethyltetraselenafulvalenium perchlorate [$(TMTSF)_2ClO_4$] at low temperatures in fields up to 31 T. Above the cascade of field-induced spin-density-wave transitions, the system remains in a remarkably stable semimetallic state, with constant Landau filling factor (ν), from 8 to 27 T. The measurements indicate that this state is related to the $\nu=\frac{1}{3}$ fractional quantum Hall effect. At 27 T there is a new transition, to a novel state, distinct in its behavior from the lower-field transitions.

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The Bechgaard family of charge-transfer salts [$(TMTSF)_2X$ where TMTSF is tetramethyltetraselenafulvalene and $X=ClO_4$, PF_6, ReO_4, etc.] are anisotropic organic conductors which exhibit the rich phase characteristics of an interacting quasi-2D electron gas. Initial interest in $(TMTSF)_2ClO_4$ arose as it was the first ambient-pressure organic superconductor.[1] Subsequent interest has focused on the unique series of magnetic-field–induced transitions (MFIT) in this material.[2] At low temperatures $(TMTSF)_2ClO_4$ is superconducting below 0.1 T, and a normal metal up to the threshold field ($H_{th}\simeq 4.5$ T at 0.7 K) where there is a second-order spin-density-wave (SDW) transition to a semimetallic state. From H_{th} to 8 T, $(TMTSF)_2ClO_4$ undergoes a cascade of first-order MFIT between distinct semimetallic SDW phases. These transitions have been well characterized, and several recent theories[3-7] provide a good (at least qualitative) understanding for the mechanism involved. However, these theories all predict a final transition at $\simeq 8$ T to a high-field semiconducting state.

We have measured longitudinal resistance (ρ_{xx}), Hall resistance (ρ_{xy}), and magnetization in fields up to 31 T using the hybrid magnet at the Francis Bitter National Magnet Laboratory. We find that, at 0.7 K, $(TMTSF)_2ClO_4$ remains semimetallic, with a constant Landau filling factor (ν), from 8 to 27 T. The behavior of this unpredicted, remarkably stable state leads us to associate it with the $\nu=\frac{1}{3}$ fractional quantum Hall effect (FQHE).[8] At 27 T there is a very-high-field transition[9] (VHFT) to a novel state, which distinguishes itself from the "low-field" transitions by its opposite temperature dependence, dramatic increase in ρ_{xx}, sharp decrease in ρ_{xy}, and weak anomaly in the magnetization.

Single crystals of $(TMTSF)_2ClO_4$ are electrochemically grown from solution with typical dimensions of $5\times0.3\times0.2$ mm^3. The low-temperature mean free path in a particular $(TMTSF)_2ClO_4$ sample can be adjusted by the rate at which it is cooled through a structural transition near 24 K. Quenched (Q) samples ($\Delta T/\Delta t > 1$ K/sec) undergo an SDW transition in zero field at 4 K, and are insulating at low temperatures. Only relaxed (R) samples ($\Delta T/\Delta t < 1$ K/min) exhibit superconductivity and the MFIT. Very relaxed samples ($\Delta T/\Delta t < 100$ mK/min) have mobilities in excess of 10^5 cm^2/sec·V,[10] and additional field-induced phases.[11] We have measured numerous samples with various cooling rates. All non-Q samples exhibit qualitatively similar behavior above 8 T.

Magnetization measurements were made with a small-sample force magnetometer.[12] Transport measurements were made with six 1-mil Au wires (two wires for current and four wires for various voltage configurations) attached with Ag paint. Sample inhomogeneities make it impossible to obtain perfect Hall contacts, and so measurement of ρ_{xy} requires field inversion. Since the direction of the field in the hybrid magnet cannot be changed, we constructed a flipping probe to invert the samples. Samples could be rotated a full 360° with less than 1% reproducibility error.

The transport data reported here were taken on two samples, No. 1 and No. 2, which were both cooled twice from 26 to 10 K: at an average rate of 60 mK/min (*RR* state) and 6 mK/min (*RRR* state). As judged by their relative resistivities, sample No. 1 was a typical sample, whereas No. 2 was an exceptionally high-quality sample. The magnetization data were taken on a third sample cooled at 12 mK/min.

Figure 1 shows ρ_{xx} and ρ_{xy} in fields up to 20 T for sample No. 2*RRR* at 0.7 K. The steps in ρ_{xy} and the minima in ρ_{xx} are reminiscent of the quantum Hall effect,[13] but several features[10,11] distinguish it from the usual QHE. Briefly, the Hall plateaus are not $\propto h/\nu e^2$ [(25.8... kΩ)/ν per layer], ρ_{xx} *increases* sharply during the first few plateaus, the steps are not periodic in $1/H$, the field at which each step occurs (as well as the num-

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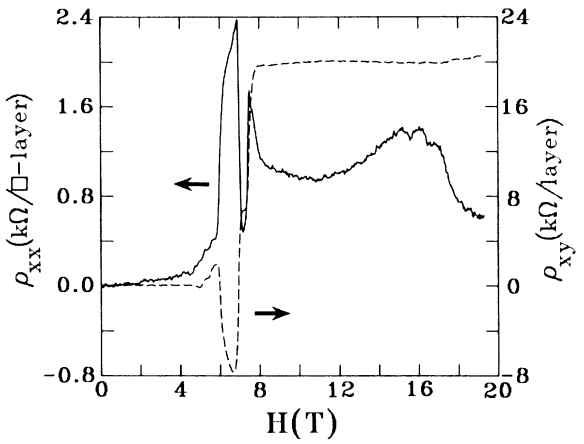

FIG. 1. Hall (dashed) and longitudinal (solid) resistivities for $(TMTSF)_2ClO_4$ sample No. 2*RRR* at 0.7 K in fields up to 20 T. A brief shoulder at 7.5 T coincides with a sharp reduction in ρ_{xx}. The ratio of ρ_{xy} from this shoulder to the high-field plateau is $1:(2.96\pm0.05)$ for all samples measured, suggesting that the shoulder corresponds to $\nu=1$ and the high-field plateau has $\nu=\frac{1}{3}$.

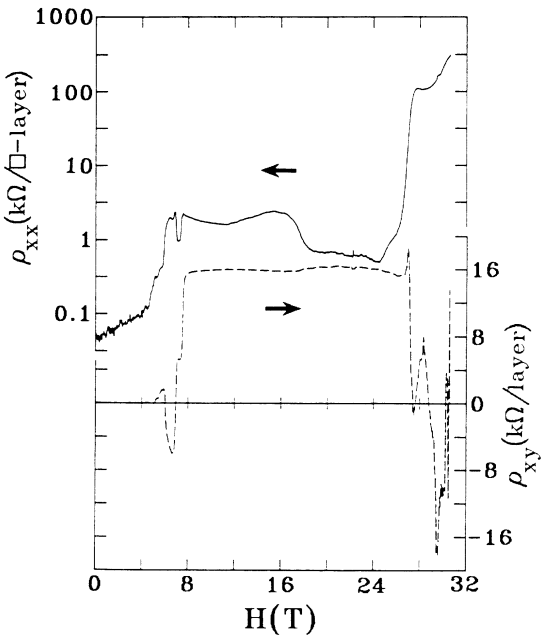

FIG. 2. Hall (dashed) and longitudinal (solid) resistivities for sample No. 2*RR* at 0.7 K in fields up to 31 T. The high-field plateau persists out to 27.1 ± 0.1 T where a sharp decrease in ρ_{xy} and dramatic increase in ρ_{xx} (note logarithmic scale) define the VHFT.

ber of steps) is temperature dependent, and there is distinct hysteresis between the up- and down-field sweeps. Thermodynamic measurements[14,15] show that, in fact, the Hall steps between H_{th} and 8 T are due to first-order phase transitions.

The $(TMTSF)_2ClO_4$ crystal consists of rectangular TMTSF molecules stacked along the **a** axis. The conduction bandwidths have the approximate ratio 100:10:<1 in the **a**:**b***:**c*** directions. The Fermi surface consists of two warped planes about $k_a=\pm\pi/2a$. Although $(TMTSF)_2ClO_4$ is highly anisotropic, the **b*** bandwidth of high-purity samples in low fields is sufficient to suppress the usual 1D instabilities. For fields parallel to **c***, the net electron motion is along the **a** axis, with oscillatory motion in the **b*** direction.[3,6] With increasing field, the **b*** motion decreases, thereby enhancing the 1D character of the electrons. At H_{th} the Fermi-surface nesting becomes sufficient to favor formation of a SDW.

Existing theories[3-7] for the MFIT in $(TMTSF)_2ClO_4$ consider the field dependence of the particular SDW distortion which gives the lowest net energy. Transitions occur when a new distortion becomes favorable, and the system discontinuously readjusts the SDW to keep E_F in the largest gap. As a result of incomplete nesting, the self-consistent SDW potential leaves pockets of electrons and holes, which quantize into discrete Landau levels. The intense fields cause considerable magnetic breakdown, which connects the electron and hole pockets. Thus, even in the absence of impurities, the discrete levels are broadened into Landau bands. Since E_F is pinned in a gap between bands (to gain the maximum SDW condensation energy), the 2D electron system should exhibit quantized Hall plateaus. A recent theory,[16] however, suggests that impurities may cause increased longitudinal resistance and Hall plateaus which maintain their proper ratios but which have reduced absolute values compared to closed-orbit QHE systems, as is observed.

The existing theories predict that E_F should go to the single remaining large gap at the last MFIT (usually taken to be the transition near 8 T), above which the system should be semiconducting. Figure 2 shows that, at 0.7 K, $(TMTSF)_2ClO_4$ remains semimetallic from 8 to 27 T. Furthermore, the fact that ρ_{xy} is constant over this extraordinarily large region shows that the carrier density changes in such a way as to maintain a fixed Landau filling. Insight into the origin of this unpredicted, remarkably stable state comes from the relative values of ρ_{xy}. Theoretically one expects the ratio of $\frac{1}{3}:\frac{1}{2}:1$ for the three steps preceding the 8-T transition. Indeed, neglecting the anomalous negative step (indicative of ultrapure samples), Ribault[17] finds this ratio to be 0.36:0.5:1. Furthermore, he finds that the ratio for the 8-T step is 1:2.9. In the present study, the magnitudes of the high-field plateaus are 18 ± 1 kΩ/layer, 17 ± 1 kΩ/layer, and 14 ± 1 kΩ/layer for samples No. 2*RRR*, No. 2*RR*, and No. 1*RRR*, respectively, whereas the ratio for the 8-T step is $1:(2.96\pm0.05)$ regardless of sample purity. The combination of constant ρ_{xy} with this universal step size strongly suggests that the carriers are in a FQHE state with $\nu=\frac{1}{3}$. It should be noted, however, that "conventional" FQHE is not expected since

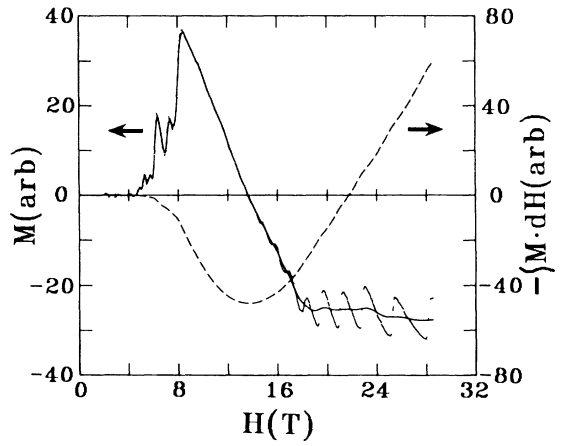

FIG. 3. Magnetization of $(TMTSF)_2ClO_4$ at 0.7 K (points). The paramagnetic steps above 14 T are not associated with the VHFT. Use of a Fourier filter to remove these steps (solid) reveals a small *diamagnetic* step. The magnetic energy ($E_M = \int \mathbf{M} \cdot d\mathbf{H}$, dashed) becomes positive above $\simeq 22$ T.

$(TMTSF)_2ClO_4$ has neither a fixed carrier density nor fixed E_F; it has the additional freedom to choose a nesting vector which places E_F in the configuration with the lowest total energy.

Independent support for the fixed Landau filling and extreme stability of the state from 8 to 27 T comes from the magnetization measurements, Fig. 3. All of the "low-field" MFIT are signaled by a paramagnetic jump, followed by a brief diamagnetic recovery which never takes the magnetization to a net diamagnetic value. Following the 8-T transition the magnetization decreases linearly, crossing zero at 14 T. The paramagnetic steps above $\simeq 14$ T can be ascribed to de Haas–van Alphen oscillations from quantized edge states,[18] and are not associated with any phase transitions.[19] Use of a Fourier filter to remove these oscillations reveals that the intrinsic (bulk) magnetization decreases linearly from 8 until 18 T, where it saturates to a negative value. The linear diamagnetic term is most readily related to a fixed Landau filling. For such a system the Landau degeneracy and level energies both vary as H; hence the net energy increases as H^2 and the magnetization decreases linearly with field.[20] The net magnetic energy of $(TMTSF)_2ClO_4$ (dashed curve in Fig. 3) becomes positive above $\simeq 22$ T,[21] but the $\nu = \frac{1}{3}$ state persists until 27 T. Finally, the system must find a new ground state.

Several features distinguish the VHFT from the cascade of low-field MFIT. First, ρ_{xx} increases dramatically, nearly 3 orders of magnitude from 25 to 30 T at 0.7 K. Second, ρ_{xy} *decreases* sharply. (Rapid variations in ρ_{xx} induce a sizable uncertainty in ρ_{xy}, but our exhaustive investigation of more than a dozen samples, including measurements above 1 K where ρ_{xx} does not diverge so dramatically, has convinced us that ρ_{xy} does indeed decrease sharply, to 0 ± 5 kΩ/layer above 28 T.) Third, the VHFT has a negative field slope; the field at which the transition occurs *decreases* with increasing temperature. Finally, there is no conspicuous paramagnetic anomaly associated with the VHFT; in fact, careful inspection of the filtered data in Fig. 3 reveals a slight *diamagnetic* step.

The behavior above the VHFT is indicative of a localized-electron system. The temperature dependence of the longitudinal resistivity infers activated conduction with a gap of $\simeq 4$ K. Divergent ρ_{xx} with finite ρ_{xy} is characteristic of magnetic-field–induced metal-insulator transitions.[22,23] Wigner[24] localization in very high fields is predicted to be weakly first order,[25] with a negative field slope[26] and saturated diamagnetism,[27] consistent with what is seen. An alternative explanation could be strong localization due to the enhanced 1D character of the electrons in these fields.

Existing theories for the high-field behavior of $(TMTSF)_2ClO_4$ have not considered the direct Coulomb interactions between electrons. Many-body interactions are essential for the formation of the FQHE state (as we presently understand it[28]), and for the majority of electron localization mechanisms. Their neglect may explain why the $\nu = \frac{1}{3}$ state from 8 to 27 T and the novel state above 27 T were unpredicted.

In conclusion we have made magnetotransport and magnetization measurements on $(TMTSF)_2ClO_4$ in fields up to 31 T. We find an unpredicted, extraordinarily stable state from the final low-field spin-density-wave transition at 8 to 27 T. This novel state has a fixed Landau-level filling which we associate with the $\nu = \frac{1}{3}$ fractional quantum Hall effect. At 27 T there is another transition to a new phase, with divergent longitudinal resistivity and small Hall resistivity. The behavior above 27 T is consistent with the formation of a localized-electron system.

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