Quantized Hall effect in the organic superconductor (TMTSF)$_2$ReO$_4$

(TMTSF=tetramethyltetraselenafulvalinum)

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We report evidence for a well-defined quantum Hall effect in the field-induced spin-density-wave states of the organic superconductor (TMTSF)$_2$ReO$_4$. Hall resistance plateaus at $h/2e^2$ and $h/4e^2$ were clearly identified and correspond to the $n=1$ and $n=2$ states of the standard quantized nesting model. Magnetic breakdown is proposed as a tentative interpretation for the change in behavior of the Hall voltage occurring around 16 T and the existence of fast magnetoresistance oscillations. It is found that even in the semiconducting $n=0$ phase the absolute value of $\rho_{xy}$ remains of the order of $h/e^2$. A tentative explanation for this effect in terms of incipient field induced localization is proposed.

Organic superconductors (TMTSF)$_2X$ [TMTSF: tetramethyltetraselenafulvalinum, $X=\text{PF}_6$, $\text{ClO}_4$, $\text{ReO}_4$, ...] have been widely studied for the last decade. Studies under a high magnetic field have attracted particular interest. When the sample is superconducting, the application of a magnetic field first restores the normal state and then induces a series of transitions between various field-induced spin-density-wave (FISDW) phases above a threshold field. It has been understood that the magnetic field effectively reduces the dimensionality of the system and that the periodicity imposed by the magnetic field creates a series of Landau gaps around the Fermi energy, $E_F$. Since the energy gain is maximum when $E_F$ lies in the largest gap for a given field, the longitudinal component of the spin-density-wave (SDW) wave vector $Q_\parallel$ increases linearly with increasing field in order to keep $E_F$ in this gap and then suddenly jumps to a lower Landau gap. As a result, a series of phase transitions occurs until $E_F$ lies in the last gap without any filled Landau band inside. In each FISDW phase, the Hall voltage exhibits a quantized value of $h/2ne^2$ per molecular layer as in the normal quantum Hall effect (QHE), taking into account a spin degeneracy.

Observation of these effects were made for a slowly cooled sample of (TMTSF)$_2\text{ClO}_4$ under a magnetic field below 8 T. Steps with integer ratios between phases were found, but there were regions of Hall sign reversal and the step heights were far less than that expected by the theory. In subsequent experiments at higher magnetic fields, instead of finding the $n=0$ state as predicted by the quantized nesting model, an unusually wide Hall plateau was observed up to 25 T, which has been claimed to be a fractionally quantized state. An unexpected reentrance into the metallic state has been observed above 25 T. Recently, similar Hall steps have been observed in (TMTSF)$_2\text{PF}_6$ under pressure. In (TMTSF)$_2\text{PF}_6$, not only were integrally quantized Hall plateaus observed but the height of each plateau also agreed quantitatively with the theoretical value $h/2ne^2$ in one of the investigations. Moreover, the $n=0$ state predicted by the quantized nesting model was found above 18 T. Consequently, the quantized Hall effect found in (TMTSF)$_2\text{PF}_6$ seems to be well explained by the quantized nesting model.

The difference between (TMTSF)$_2\text{PF}_6$ and (TMTSF)$_2\text{ClO}_4$ was attributed to the absence of the anion-ordering transition which occurs around 24 K in the latter compound. Namely the $b$ lattice parameter of the ClO$_4$ salt is doubled below 24 K. This causes the open Fermi surface to be folded back into the smaller Brillouin zone giving two intersecting sheets. These sheets hybridize at their intersection (near $k_F = 0$) giving two open surfaces. If the hybridization energy is small compared with $4t_b$ where $t_b$ is the transverse transfer integral then the Fermi surface will only be slightly modified. The anion-ordering gap was suggested as the origin of the “fast” oscillations (FO’s) found in (TMTSF)$_2\text{ClO}_4$ salt over the entire field range. However, the observation of the same kind of oscillations in (TMTSF)$_2\text{PF}_6$ salt under ambient pressure and also in $n=0$ phase above 2 K makes this argument somewhat uncertain.

FISDW transitions and FO’s are also observed in (TMTSF)$_2\text{ReO}_4$ under pressure. The latter magnetoresistance (MR) study showed very prominent FO’s both below and above the threshold field as in (TMTSF)$_2\text{ClO}_4$. Under ambient pressure, (TMTSF)$_2\text{ReO}_4$ undergoes a metal-insulator phase transition due to anion ordering which doubles the unit cell in all crystalline directions ($Q_1 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$). Upon applying pressure, the transition temperature decreases and superconductivity was observed beyond 10 kbar. Studies of the anion-ordering phase diagram by x-ray diffraction revealed that another kind of anion ordering of wave vector $Q_2 = \left(0, \frac{1}{2}, \frac{1}{2}\right)$ appears beyond 8 kbar.
Provided that we neglect the small effect of the crystalline c direction on the electronic structure, under a pressure $P_c$ large enough to suppress $Q_1$ ordering, $(\text{TMTSF})_2\text{ReO}_4$ is similar to $(\text{TMTSF})_2\text{ClO}_4$ in its relaxed state in that the unit cell doubles in the $b$ direction. The existence of FO's over the whole field range is also similar to $(\text{TMTSF})_2\text{ClO}_4$.

In the work reported here, a platelike single crystal ($2.5 \times 0.5 \times 0.2 \text{ mm}^3$) of $(\text{TMTSF})_2\text{ReO}_4$ was placed in the Teflon cell of a miniaturized Be-Cu pressure clamp. Experimental details were as reported before. The experiments above 12 T were performed at the Service National des Champs Intenses, Grenoble, France. The pressure needed to stabilize a metallic state required about 3 kbar more than for $(\text{TMTSF})_2\text{PF}_6$.

Although the same nominal pressure has been used for all experiments (13.5 kbar at room temperature), we obtained two distinct resistance behaviors, one with a resistance peak around 60 K and the other with a monotonic resistance decrease and a change in slope near 100 K similar to that in ClO$_4$ near 24 K. We believe that the pressure on the sample was slightly above or slightly below $P_c$ depending on the pressure loss on cooling through the solidification point of isopentane. The data reported here were obtained for a sample with a slope anomaly, i.e., near $P > P_c$.

Magnetoresistance and Hall-effect data taken in the hybrid magnet at 0.5 K are shown in Fig. 1 and Fig. 2, respectively. Also shown as an inset of Fig. 1 is the magnetoresistance between 4 and 8 T which shows FO's reminiscent of those in Ref. 11. ($H_{FO} = 320$ T.) First, we will focus on the results above 16 T. We obtained two well-defined Hall plateaus with ratio $1/2$:1. At 22.3 T occurred the last transition to the very resistive state, which was identified by the rapid change of MR. This behavior is very similar to the transition to $n = 0$ phase in $(\text{TMTSF})_2\text{PF}_6$. The heights of Hall plateaus correspond quantitatively to the theoretical value of $h/2ne^2$ with $n = 1$ and 2. Namely, the largest plateau has a Hall resistance of 13.2 kΩ per molecular layer. The magnetic phase diagram thus obtained is presented in Fig. 3. The fields for transitions (open circles in Fig. 3) are defined by the resistance peaks wherever these are well defined and by the sharp increase of resistance towards the highly resistive state above 16 T. Open squares ($\square$) in the diagram of Fig. 3 show the fields where the Hall voltage reverses its sign from negative to positive. The inset of Fig. 3 shows the positions of the transition fields above

**Fig. 1.** Magnetoresistance of $(\text{TMTSF})_2\text{ReO}_4$ at 0.5 K vs magnetic field along the $c^*$ direction. Inset: oscillatory behavior of the magnetoresistance at low fields.

**Fig. 2.** Hall resistance of $(\text{TMTSF})_2\text{ReO}_4$ at 0.5 K vs magnetic field along the $c^*$ direction.

**Fig. 3.** Phase diagram for $(\text{TMTSF})_2\text{ReO}_4$ obtained in the present work. The points taken from the maximum slope on log$_{10} \rho_{xx}$ vs $H$ plots are shown by open squares for the transition to the high-field state. Open circles are taken from peaks in $\rho_{xx}$ and open triangles from the fields where the Hall voltage goes from negative to positive. Solid circles are the threshold fields where there is the first detectable increase in $\rho_{xx}$ and/or $\rho_{xy}$. 
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16 T in 1/H as a function of integers. For the PF₆ salts, all the transitions observed from n = 0 to n = 5 obeyed the Hₙ = H₁/(n + γ) law with H₁ = 60 T and γ = 3.2. According to the standard quantized nesting model which predicts this behavior the value of H₁ corresponds to the deviation from perfect nesting (i.e., the area of unnested pockets) at H=0. Smaller (higher) values of H₁ and γ correspond to better (worse) nesting and permit a state with given quantum number to be attained at lower (higher) magnetic fields. It is clear from the phase diagram in Fig. 3 that we can divide the transitions into two different regions. Above 16 T, the behavior of the present compound resembles that of the PF₆ salt; the field of transitions follow the Hₙ = H₁/(n + γ) law, although with H₁=111±3 T and γ=4.9±0.2.

Below 16 T, positive and negative Hall voltages are observed, so the standard Hₙ = H₁/(n + γ) picture will not necessarily apply. However, some standard law can still be found by plotting the reciprocal field where Hall voltage goes from negative to positive at increasing field with H₁=33 T and γ≈0.65. We may tentatively propose an interpretation for the change of behavior occurring around 16 T. This feature is probably connected with the presence of anion ordering and the fact that the Fermi surface has two open sheets in the anion-ordered state (See Fig. 4.) Depending on the nesting vector, electron pockets (A) or hole pockets (B) can be formed. The doubling of the superlattice tends to reduce the area of the hole pockets and hence an n = 2 hole pocket occurs at lower fields than the n = 2 electron pocket. However, the situation illustrated by Fig. 4 becomes no longer valid above, say, 16 T. Although magnetic breakdown is a tunneling phenomenon which develops smoothly, like exp(H/H₀), as the magnetic field is increased above a characteristic breakdown field H₀, it could easily tip the balance between the two different types of nesting vector giving hole or electron pockets. Above 16 T the magnetic breakdown is too strong to allow the small hole pockets to be formed and the 2b superlattice no longer has any effect. A value of H₀ ~ 16 T would be required for this, corresponding to a hybridization gap associated with anion ordering of Eₔ ≈ 140 K, approximately 0.25 of the transverse bandwidth 4tₖ.

The magnetic breakdown through the hybridization gap referred to above is of a rather unusual type between two parallel open orbits which would intersect in the absence of hybridization. It has been reviewed by Pippard under the heading of interferometer oscillations. Namely the phase difference between the two possible electron orbits makes the magnetic breakdown periodic in 1/H. The periodicity is defined by the k-space area enclosed by the two intersecting orbits. In the present case this area is π²tₖ/abₐ, corresponding to a breakdown frequency of 223 T. This is extremely close to the frequency of the FO’s observed in several Bechgaard salts, including ReO₄, and whose origin is presently not understood. A characteristic feature of these interferometer oscillations in normal metals is that to first order they should not be evident as de Haas–van Alphen oscillations in the magnetic susceptibility or other thermodynamic properties. However, in the Bechgaard salts this restriction will only apply in the metallic phase well away from the SDW phase boundary because otherwise magnetic breakdown will alter the free energy via its effect on the nesting properties.

According to this picture, fast magnetoresistance (MR) oscillations can occur when there is a period doubling (or any superlattice) along the b direction which causes the Fermi surface to form two or more intersecting sheets. For the ClO₄ and ReO₄ anions this can be caused by anion ordering so there can be fast MR oscillations even in the metallic region, but as mentioned above thermodynamic oscillations can only occur near to the boundary or in the FISDW phases. For the centrosymmetric PF₆ anion the superlattice must come from a commensurate SDW (or charge-density wave). Thus one could only expect to see the fast oscillations in the SDW phases and not in the metallic region. This does seem to be the case experimentally both from our work under pressure and that of Ulmet et al. at ambient pressure and very high fields.

Although the above picture involving magnetic breakdown is a viable one, direct comparison of the results presented here with previous work on PF₆ (Refs. 6 and 7) under pressure and ClO₄ (Refs. 4 and 10) at atmospheric pressure raises some interesting points.

Firstly, the Hall-effect data for PF₆ often showed positive peaks which can be seen as a tendency to form positive plateaus, especially between the negative n = 2 and n = 3 steps and also at n = 5. This was tentatively ascribed to higher-order commensurability effects following

![Diagram](image)

**FIG. 4.** (a) Scale drawing of one side of the open Fermi surface of (TMTSF)₂X in the absence of an anion superlattice. Different nesting vectors can leave electron (A) or hole (B) pockets. (b) Doubling of Fermi surface due to the halving of the Brillouin zone in the b* direction. A hybridization gap is formed at the zone center and reduces the area of the hole pockets. The electron pockets are not affected by the hybridization gap but could be affected by zone boundary effects.
the theory developed by Héritier.\textsuperscript{16} Thus an alternative interpretation of the positive Hall plateau in ReO$_4$ salt is to ascribe it to the same type of commensurability effect stabilized by the anion superlattice. Note that the two points of view are not necessarily inconsistent, since higher-order commensurability and magnetic breakdown are closely linked.

Secondly, in the proposed $n = 0$ phases of the ReO$_4$ salt at high fields, we again find that the Hall resistivity ($\rho_{xy}$) is much less dependent on magnetic field than the magnetoresistivity ($\rho_{xx}$) and again its magnitude, which is $h/2e^2$ to $h/e^2$ per layer, is in the range expected for the QHE. Plots of $\log_{10}$ $\rho_{xx}$ versus $1/T$ at 27 T show an activated behavior and a tendency toward saturation below 2 K as found for PF$_6$.

Therefore, in the light of these results it now seems to us that even in the $n = 0$ phase the Hall resistivity does not become arbitrarily large as might be expected, but is approximately field independent and of order $h/e^2$ per molecular layer. This may actually be the underlying cause of the saturation in $\rho_{xx}(H)$ at low $T$. In a simple model of an isotropic two-dimensional semiconductor, the above condition corresponds to the condition that the radius of an electron (or hole) orbit be of the same order as the mean distance between electrons.

Remember that $kT \leq \hbar \omega_c$ where $\hbar \omega_c$ is the cyclotron energy so that one only has to consider the lowest cyclotron orbit. The above condition is thus a sign that the electrons are starting to become localized and presumably the SDW gap then becomes smaller, in order to prevent this energetically unfavorable situation. In other words the ratio of the cyclotron orbit to the average distance between carriers is not allowed to become arbitrary small in the $n = 0$ state. Rather it becomes fixed at a value corresponding to one carrier per flux quantum, or $\rho_{xy} \sim h/e^2$, which prevents further carrier localization by the magnetic field.

In summary, we have carried out Hall-effect measurements in the FISDW phases of the Bechgaard salt (TMTSF)$_2$ReO$_4$. Plateaus at $h/2e^2$ and $h/4e^2$ were clearly identified and correspond to the $n = 1$ and $n = 2$ states of the standard quantized nesting model. We have tentatively proposed several additions to this model to account for some previously unexplained effects. The magnetic breakdown could be responsible for the FO's and for the change in behavior occurring around 16 T. It is found that even in the semiconducting $n = 0$ phase $\rho_{xy}$ remains of the order of $h/e^2$. This is attributed to a decrease in the SDW gap in order to maintain approximately one carrier per flux quantum and prevent field-induced localization. Within this picture, the PF$_6$ and ReO$_4$ salts have essentially similar characteristics, at least in the high-field limit ($n=0,1$).

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