Tetramethyltetraselenafulvalenium Perchlorate, $(TMTSF)_2ClO_4$, in High Magnetic Fields

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The Hall effect and the magnetoresistance of $(TMTSF)_2ClO_4$ have been measured at temperatures from 0.08 to 10 K and in magnetic fields to 22 T. The low-temperature data suggest a series of transitions induced by an orbital effect from the magnetic field which progressively reduce the carrier density. Oscillations, apparently Shubnikov–de Haas, also are observed above 10 T and at temperatures up to 10 K.

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The $(TMTSF)_2X$ family of organic conductors has an intriguing set of phase diagrams in temperature, pressure, magnetic field, and anion composition space. At room temperature these salts are metallic[1] but the ground states vary from metal to superconductor,[2] spin-density wave (SDW),[3] or anion-order–induced charge-density wave (CDW)[4] depending on the particular anion and the pressure. At low temperature, crystals which remain metallic have extraordinarily large anisotropic magnetotransport coefficients[5] especially in light of the band structure[6] which predicts only open orbits. Perhaps the most unusual phenomenon observed in these materials is found only in the metallic state at temperatures below ~10 K. Here, when a magnetic field is applied along the c^* direction, "oscillations" are induced in many of the properties as the field is increased beyond a "threshold field." This effect was first discovered in the PF_6 salt.[7] Recent work on the ClO_4 salt[8] has shown that the state found above the "threshold field" is magnetic in character, similar to the SDW state observed in the insulating state.[9] However, a detailed understanding of the nature of the field-induced state and exactly how the magnetic field induces such a state is lacking.

To learn more about the field-induced state we have made the first measurements of the Hall effect and magnetoresistance in $(TMTSF)_2ClO_4$ at fields up to 22 T and temperature down to 80 mK.[10] The Hall data at 80 mK correspond to an effective carrier concentration at 15 T which is ~200 times smaller than that calculated from the stoichiometry. However, this apparent decrease in carriers does not appear abruptly above the onset field but occurs as a series of steps, as one would expect from a series of transitions to semimetallic states with increasingly lower electron density.

Another important finding is the presence of "real" Shubnikov–de Haas (SdH) oscillations above 10 T. These oscillations appear even above 5 K, where no threshold can be identified. The frequency of the oscillations suggests the presence of closed orbits encompassing 3.4% of the Brillouin-zone a-b plane.

The experiments were performed in two apparatus at the Francis Bitter National Magnet Laboratory. One setup used a He^3 cryostat capable of 0.5 K in conjunction with a 22 T magnet and the other a dilution refrigerator capable of 80 mK in a 15 T magnet. The samples were mounted on 13- or 25-μm gold wires with Ag paint. Two current leads were placed on the ends of the rectangular platelike crystals (current along the highly conducting a axis) and two additional leads were placed on each of the long edges of the samples so that the Hall effect (a-b plane) and magnetoresistance could be obtained simultaneously. Hall measurements were done at 27 Hz with typical currents of ~ 500 μA and resulting maximum voltages of 250 μV at low temperature and high field. Typical sample dimensions were 5 mm ×0.3 mm× 35 μm. The samples were aligned by eye so that the magnetic field was parallel to the crystallographic c axis.

$(TMTSF)_2ClO_4$ is superconducting and has large magnetotransport coefficients at low temperatures only when it is slowly cooled through the anion-ordering temperature (24 K).[8,11] Quick cooling ("quenching") results in a SDW transition at ~ 5 K.[11] The present samples were cooled from 40 to 4 K at a rate of less than $\frac{1}{2}$ K/min, and showed a monotonic decrease in resistance as temperature was lowered from 40 to 0.08 K.

In Fig. 1 we show the resistance measured in the magnetoresistance and Hall configurations plotted versus applied field. At 0.5 K the magnetoresistance is substantial, but the Hall resistance R_{xy} is too small for our sensitivity, up to the threshold field (~ 5 T). Above this field the resistance increases more rapidly and the Hall coefficient becomes observable. R_{xy} remains small until 6.4 T at which point there is another rapid increase and leveling off until 8 T. At this point R_{xy} again rapidly increases and then remains fairly level above 12 T. This behavior in R_{xy} is characteristically different from the variations about a straight line ($R_{xy} \propto H$) which would be expected for the SdH effect or the quantum Hall effect (QHE).[12] On the other hand 80-mK data (Fig. 2), which show five jumps between 3.25 and 8 T, indicate that the jump positions are roughly periodic in $1/H$ with a frequency of ~ 23 T. (We note that an expected Hall jump at 11.4 T is conspicuously absent.)

We have measured three samples to 0.5 K and 22 T and two samples to 80 mK and 15 T. All of these samples showed the same Hall resistance to within our uncertainty of orientation and sample dimensions (± 15%). The stepwise increase in R_{xy} suggests some manifestation of the QHE. For comparison we have indicated the Hall resistivity in terms of h/e^2 per conducting plane in Fig. 1. However, the non-"consecutive integer" ratio of the plateaus of R_{xy}, their temperature dependence, and the absence of a significant lowering of R_{xx} indicate that a single-carrier QHE is not sufficient to explain our results.

The Hall coefficient is positive and gives the effective number of carriers as 7×10^{18} holes/cm^3 at 20 T and 0.5 K. This value is both field and temperature dependent as shown in Fig. 3.

The threshold field versus temperature for all measurements on all of the samples used in this study is shown in the upper inset of Fig. 4. Previous limited measurements agree with the present more extensive data. The washing out of the magnetic-field–induced transition above 5 K is illustrated by the data shown in Fig. 4, where we have plotted the magnetoresistance at temperatures of 4, 7, and 10 K. What is even more intriguing in this figure are the oscillations of the resistance, seen at high fields at all of the temperatures shown as well as at lower temperatures. The positions of the maxima in these os-

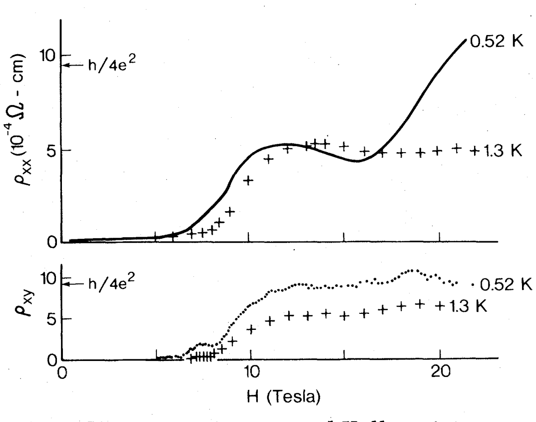

FIG. 1. Magnetoresistance and Hall resistance as functions of magnetic field at 0.52 and 1.3 K. Resistance is also labeled in terms of h/e^2 per conducting plane. At 0.52 K, $R_{xx}(20\ \mathrm{T})/R_{xx}(2\ \mathrm{T}) \sim 250$.

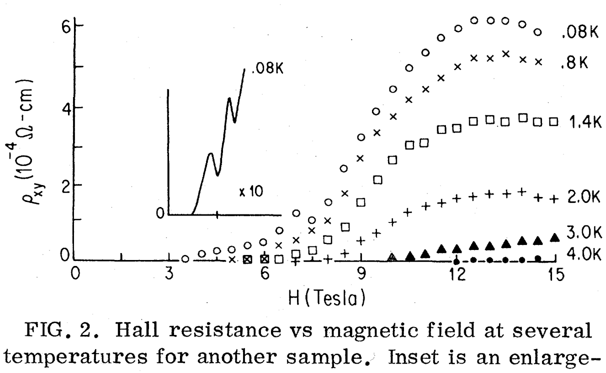

FIG. 2. Hall resistance vs magnetic field at several temperatures for another sample. Inset is an enlargement of the threshold region.

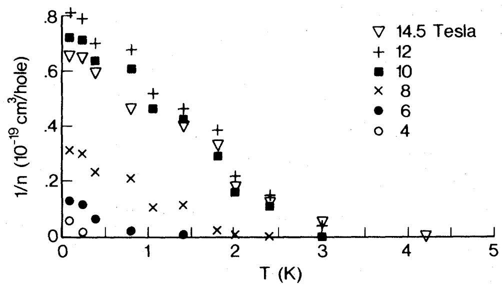

FIG. 3. Temperature dependence of the Hall coefficient (plotted as inverse effective carrier density) at various fields.

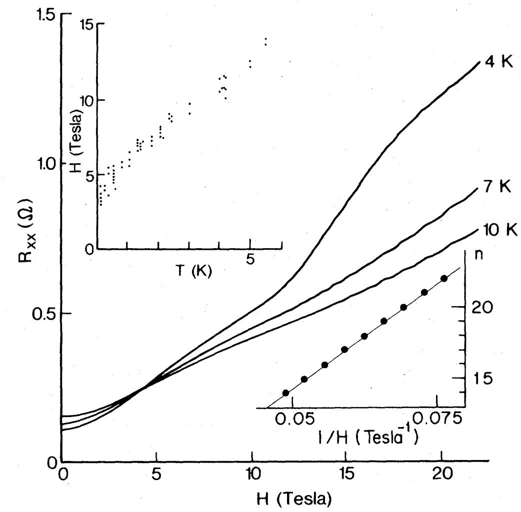

FIG. 4. Magnetoresistance vs magnetic field at 4, 7, and 10 K. Note oscillations at high field. Upper inset: Temperature dependence of the threshold field for all of the samples investigated in this study. Lower inset: Positions of the maxima from the 7 K data vs $1/H$.

cillations plotted vs $1/H$ (lower inset Fig. 4) yield a straight line characteristic of the SdH effect with a frequency of 275 ± 15 T. This frequency is ~ 10 times the frequency seen in the vicinity of the threshold field, but is very similar to one of the frequencies reported by Bando *et al.* (More often we saw a frequency of 550 T which we take as a harmonic.)

Current interpretations of the low-temperature, high-field behavior suggest that the threshold field signals a sharp transition from either open orbits to closed orbits, or from very small closed orbits to somewhat larger ones, and this is followed by "conventional" SdH oscillations.[7,8,10,14] The present study of $(TMTSF)_2ClO_4$ suggests that here the threshold field initiates a series of transitions, approximately periodic in $1/H$ (below 10 T), which progressively reduce the effective number of carriers. This interpretation is consistent with the shape and hysteresis of the magnetoresistance (observed in the present work as well as previously reported[8]), and the measured Se^{77} NMR relaxation rates,[9,15] and sound velocity[16] which show that the density of states at the Fermi surface is reduced in a roughly stepwise manner as magnetic field is increased. We note that much of this anomalous behavior has not been observed in the PF_6 salt which also has a threshold field. The high-frequency oscillations we observe may be related to the oscillations observed in the PF_6 salt. The frequency is close to that predicted for $(2k_F, 0, 0)$ nesting of the Fermi surface,[14] neglecting anion ordering.

The threshold field depends uniquely on the component of the field along the c axis.[7,13,15] Thus, unless there are enormous spin-orbit effects, the transitions are induced by an orbital effect of the magnetic field rather than spin alignment.[14] The orbital nature of these effects is also suggested by the approximate $1/H$ dependence found here.

Such orbitally induced transitions are not common. The only similar effect is the proposed CDW transition in graphite at low temperatures and in sufficient fields so that it is almost in the extreme quantum limit.[17] In such large fields the electronic structure consists of a series of distinct Landau levels each described by the quasi one-dimensional dispersion and density of states of the narrow c-axis band.[18,19] The one-dimensional band structure is susceptible to a number of distortions at $2k_F$ along c, of which, for graphite, the proposed strongest is due to a Coulomb-induced CDW.[18] The temperature dependence of the observed and predicted transition in graphite is similar to the temperature dependence of the threshold field in the present case. The dominant effect in $(TMTSF)_2ClO_4$, however, is probably some form of SDW.[9,15] The approximate $1/H$ dependence of the transitions may result from the presence of several Landau levels below the Fermi energy when the threshold field is first reached at low temperature.[19]

In conclusion we have shown that the Hall resistance increases in a roughly stepwise manner as magnetic field is increased past a threshold at low temperature, and we suggest that this is the result of a series of transitions induced by the orbital motion of the carriers in the applied field. We also observe apparent SdH oscillations at high field suggesting the presence of closed orbits with area ~ 3.4% of the a-b plane of the Brillouin zone.

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