Reentrant Field-Induced Spin-Density-Wave Transitions

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We have used magnetotransport measurements to determine the phase diagram of $(TMTSF)_2ClO_4$ from 0.5 to 10 K in magnetic fields to 30 T. This organic metal becomes a spin-density-wave semimetal as temperature is reduced in a magnetic field greater than a threshold field $H_c(T=0)\sim 3$ T. The critical temperature $T_c(H)$ increases with field in agreement with present theories, and reaches a maximum of 5.6 K at 18 T. Above this field, however, $T_c(H)$ decreases, extrapolating to zero temperature at 17 T. This reentrant phase diagram is not present in any theoretical model.

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The anisotropic organic conductors $(TMTSF)_2X$ (where TMTSF denotes tetramethyltetraselenafulvalene and $X=ClO_4$, PF_6, ReO_4, etc.), the Bechgaard salts, exhibit a wealth of physical phenomena characteristic of electron interactions in reduced dimensions.[1] Low-field ground states of these systems include insulating charge- and spin-density waves (SDW), and superconductivity.[2] Perhaps the most interesting behavior, however, is the unique series of magnetic-field–induced spin-density-wave (FISDW) transitions from "normal" metal to different semimetal phases in high magnetic fields.[3-8] The stacked platelike molecules yield a highly anisotropic two-dimensional (2D) Fermi surface with only open orbits. A perpendicular magnetic field further reduces the dimensionality toward one, and leads to an instability favoring SDW formation. In theories[9-13] of the FISDW's, the magnetic length and SDW wavelength interact to form a complex spectrum of energy gaps between Landau bands. The gaps grow, separate, and oscillate with the applied field, resulting in a sequence of phase transitions as the SDW wave vector readjusts itself to maintain the Fermi energy in the largest gap. All present theoretical treatments of these transitions predict a final high-field semiconducting state with the Fermi energy residing in the sole remaining gap. Experimental studies on the $X=ClO_4$ salt at low temperatures suggest that the final transition occurs at 8 T, but in fact, this system remains semimetallic until 26 T at 0.6 K, where there is a very high-field transition (VHFT) to a "novel" phase.[14-16]

In this Letter we report extensive magnetotransport measurements on $(TMTSF)_2ClO_4$ throughout the entire FISDW and VHFT regimes, both as a function of temperature at constant magnetic field and as a function of field at constant temperature. We find that the two transitions merge smoothly together and disappear above 5.6 K, with no indications of a multicritical point. This shows that the VHFT is actually a reentrance into the lower-field metal phase, a situation not considered by any theory extant.

The experiments were performed with use of the hybrid magnet at the Francis Bitter National Magnet Laboratory on crystals grown at Exxon. Since the field cannot be inverted in the hybrid magnet, two samples were mounted on a fully rotatable ($>360°$) platform to allow separation of the longitudinal (ρ_{xx}) and the Hall (ρ_{xy}) resistances in these highly anisotropic materials. Reproducibility of aligned and flipped ($+180°$) orientations was better than 1°. Each sample had six 1-mil Au wires attached with Ag paint for various voltage and current configurations. Simultaneous measurements of ρ_{xx} and ρ_{xy} were made with a single ac current of 0.5 mA ($\simeq 1$ A/cm^2) at 314 Hz, and two lock-in amplifiers. The samples were slowly cooled from 25 to 15 K at a rate of 7 mK/min to allow relaxation from the anion ordering transition[17] at 24 K. Temperature was controlled by a capacitance thermometer calibrated against ^{3}He and ^{4}He vapor pressures, and against a Si diode above 4 K. We present data from one sample, as both showed the essential features discussed.

In Fig. 1 we show ρ_{xx} and ρ_{xy} in fields to 30 T at several temperatures (only traces *a* and *b* are shown for fields less than 7 T). Above 6 K (curves *i*, *j*, *k*, and *l*), ρ_{xx} increases smoothly with field while ρ_{xy} remains small. Here, we ignore the Schubnikov-de Haas–type oscillations not associated with any phase transition.[5,7,14,18] At these high temperatures , there is no evidence for phase transition throughout the entire field range, and the small Hall resistance reflects metallic behavior. From 2.6 to 5.4 K (curves *c*–*h*), there is a single large-scale bump which develops in both ρ_{xx} and ρ_{xy}. This bump defines a region of increased resistance and reduced density of carriers indicative of the FISDW semimetal phase. Below 2 K, ρ_{xx} and ρ_{xy} develop

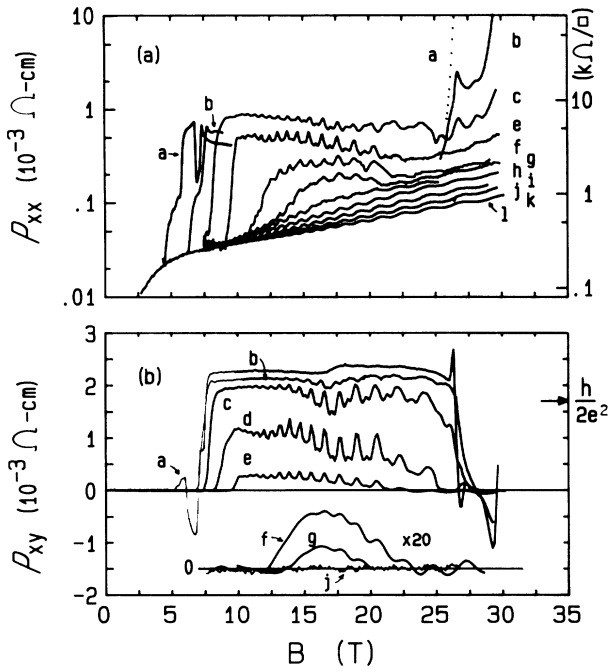

FIG. 1. (a) Magnetoresistance and (b) Hall resistance at several temperatures (note log scale for ρ_{xx}). Temperatures: trace *a*, 0.6 K; *b*, 1.4 K; *c*, 2.6 K; *d*, 3.1 K; *e*, 3.9 K; *f*, 4.5 K; *g*, 5.0 K; *h*, 5.4 K; *i*, 6.1 K; *j*, 7.2 K; *k*, 8.3 K; *l*, 9.3 K. ρ_{xx} for traces *a* and *b* decreases below 0.1 mΩ-cm between 10 and 20 T, and is not shown, while ρ_{xx} for trace *a* rises above 120 mΩ-cm at 30 T.

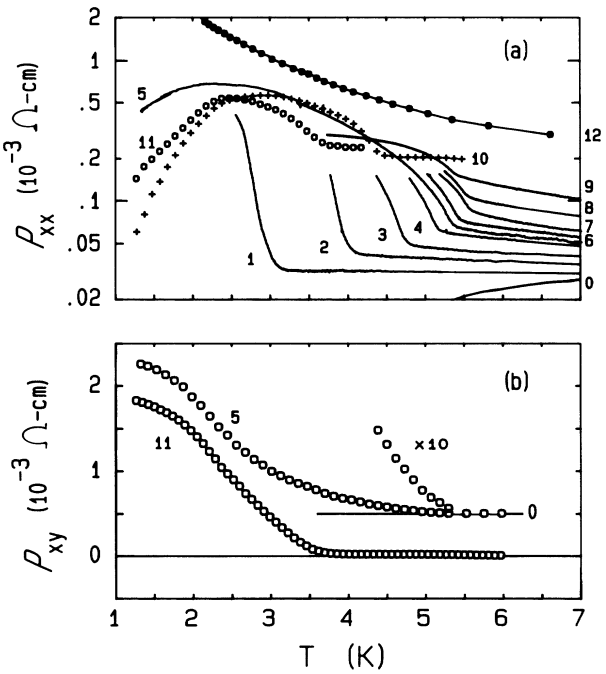

FIG. 2. Temperature sweeps at constant magnetic field, showing the FISDW-metal transition. Magnetic fields (T): trace 0, 0; 1, 8.5; 2, 10; 3, 11.4; 4, 13; 5, 14; 6, 14.6; 7, 16.9; 8, 18.1; 9, 21.6; 10, 23; 11, 25; 12, 29. ρ_{xx} in trace 0 is multiplied by 2, and in trace 12 rises smoothly to 120 mΩ-cm at 0.6 K.

several steps characteristic of the sequence of FISDW transitions from 3 to 8 T, and the remarkably stable state from 8 to 26 T which has previously been associated with the fractional quantum Hall effect.[19] This semimetallic regime develops systematically out of the metallic "background," which can be extrapolated smoothly from below the first FISDW to above the VHFT. (The negative Hall step at 6.5 T in trace *a* is an interesting anomaly first observed by Ribault,[4] and is only present in clean, well relaxed samples. Also, there is a slight change in ρ_{xy} at $\simeq$15 T which may be real, or may be due to a small contribution from ρ_{xx}. Its temperature dependence is similar to the anomaly called "$B2$" in Ref. 15.)

In Fig. 2 we show constant-field temperature sweeps of $\rho_{xx}(T)|_H$ and $\rho_{xy}(T)|_H$. At $H=0$, in the metal phase, the resistance decreases as temperature is lowered, presumably as a result of reduced scattering (curve 0). For finite fields and high temperatures, ρ_{xx} increases smoothly with decreasing temperature again presumably as a result of reduced scattering [since $\Delta\rho/\rho \propto f(\omega_c\tau)$, where $f(x)$ is a monotonically increasing function of x]. At higher fields $\rho_{xx}(T)$ clearly shows the transition at $T_c(H)$ as a sharp change in the slope $\partial\rho/\partial T$. Below this transition, the resistance increases and then decreases with decreasing temperature [see traces 5, 10, and 11 in Fig. 2(a)].

Inspection of these slope changes in Fig. 2(a) reveals an increase in transition temperature with increasing field (curves 1–6), followed smoothly by a decrease in T_c with increasing H (curves 7–11), with a maximum T_c of $\simeq$5.6 K. For fields above 26 T ρ_{xx} is again a smoothly (but rapidly) increasing function of decreasing temperature with no kinks or sharp slope changes. This is shown in trace 12 down to 2 K, and, in fact, ρ_{xx} increases to 120 mΩ-cm (1 MΩ/□) at 0.6 K. Note that outside the FISDW region $\rho_{xx}(T)$ follows a systematic variation with field, again suggesting that the very high-field and low-field states are the same "normal" metal phase. Similarly, $\rho_{xy}(T)$ is very small and relatively temperature independent at very high and low fields. As shown in Fig. 2(b), the transition at $T_c(H)$ is evident as a slope change, and the development of the amplitude of the Hall plateau can be seen as a rise from near zero at the transition to saturation at low temperature. As ρ_{xy} tends to saturate, there is a gradual drop in ρ_{xx} as expected for the quantum Hall effect.

For the purpose of constructing a phase diagram, we take in Fig. 1 the threshold field, $H_{cF}(T)$, for the FISDW as the lowest field at which the sharp rise in ρ_{xx} and ρ_{xy} occurs, and $H_{cV}(T)$ as the field at which the drop in ρ_{xy} and the rise in ρ_{xx} occur signaling the VHFT. In Fig. 2, we take as $T_c(H)$ the temperature at which ρ_{xx} and ρ_{xy} first deviate from the smooth high-

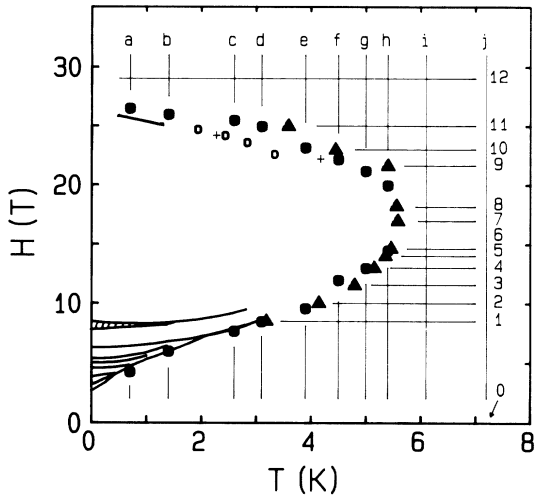

FIG. 3. Reentrant H-T phase diagram for $(TMTSF)_2ClO_4$ at high fields. Light horizontal and vertical lines represent the temperature and field excursions of Figs. 1 and 2. Solid symbols, present data; thick lines and other symbols, previous results.

temperature behavior.

The H-T phase boundary for $(TMTSF)_2ClO_4$ from these transport studies is presented in Fig. 3. The light vertical and horizontal lines indicate the paths taken on different sweeps, and are labeled according to those sweeps in the previous figures. The solid symbols are data from the present results (circles for H sweeps, triangles for T sweeps). The lines below 10 T show the previously published phase diagram, and we have included high-field data from Refs. 14 (crosses), 15 (open circles), and 16 (thick solid line). The phase boundary shows that $H_{cF}(T)$ and $H_{cV}(T)$ form a continuous curve joining smoothly at $\simeq 5.6$ K, or equivalently $T_c(H)$ is reentrant. This alone indicates that the low-temperature state at high field is the same as the low-temperature, low-field metallic state and that the FISDW's are reentrant. One can go continuously around the FISDW phase boundary. In fact, in following curves 0, i, and 12 with different field and temperature sweeps, we have gone from low field and low temperature to high field and low temperature without crossing any phase boundaries.

The question which presents itself is how such a remarkable phase boundary can exist! Theoretical treatments[9-13] which can account semiquantitatively for the FISDW's below 7.5 T do not give the correct behavior at higher fields where they predict an SDW insulator. The possible causes which have been left out of the theories include Coulomb correlations and "pair breaking" effects due to spin polarization and scattering times. Spin pair breaking is ruled out since we know from rotation studies of the VHFT that the reentrance is an orbital effect (H_{cV} and H_{cF} vary as $1/\cos\Theta$, Θ being the angle between H and the c^* axis, the normal to the 2D layers). Scattering effects may be important if for some reason $\hbar/\tau$ increased with H until it surpassed Δ_{SDW}, the spin-density-wave gap.

Another possibility is suggested by the persistence of the remarkably stable state with constant ρ_{xy} from 7.5 to 26 T at low temperature. A constant ρ_{xy} results from a fixed Landau-level filling, which in this case has been associated with the $\frac{1}{3}$-filled fractional quantum Hall effect[19] (the inverse ratio of the last few ρ_{xy} plateaus is very nearly $3:2:1:\frac{1}{3}$). Fixed filling ν would give a diamagnetic contribution to the free energy $E_{dia} = \nu g\hbar\omega_c/2 \propto H^2$ (g is the degeneracy of the Landau level) increasing the energy of the condensed state. This would introduce a diamagnetic contribution to the magnetization, linear in field, which has in fact been reported.[7,19] Integrating our magnetization data, $\int M\,dH$, we find that the diamagnetic energy equals the energy gained by the SDW transitions when $H = 25$–30 T.[19] Moreover, if we assume $\nu = \frac{1}{3}$ then $E_{dia} \sim E_{SDW} = N(0)\Delta_0^2/2$ at $H \sim 30$ T, where $N(0)$ is the density of states at E_F and Δ_0 is the extrapolated maximum zero-temperature SDW gap approximated from BCS. (The parameters of this calculation are sufficiently unknown that a filling of $\nu = 1$ is not ruled out.) Thus an explanation in terms of a fixed filling would explain the magnetization which in turn (or on its own) must result in a transition out of the condensed state. Equating the diamagnetic energy and the condensation energy results in $H_{cV}(T) \propto \Delta(T)$ at low temperature, which would explain why the upper part of the phase boundary is essentially flat as $T \to 0$. If this interpretation is correct, questions remain as to why the Fermi level is pinned at a fixed Landau filling over such a large range of magnetic field, and why the transition is back to the normal state rather than to an SDW insulator.

It is worth pointing out that although we associate the high-field, low-temperature phase with the normal state, it is an unusual normal metal. $\rho_{xx}(T)$ at 29 T appears as a smooth curve with no indications of a transition from 10 to 0.5 K, but its functional dependence is essentially activated, $\ln(\rho_{xx}) \propto H/T$. Also $\rho_{xx}/\rho_{xy} \gg 1$, a situation contrary to that of a normal metal. It is possible that the electronic states become localized by the increased one-dimensional behavior induced by the field, or by Coulomb correlations, or both. Such a continuous transition is not thermodynamic and would not be inconsistent with our phase diagram. It is also possible that there are additional phase transitions at high field below 1 K where our data are least reliable.

In summary, we have presented a new phase diagram for the low-temperature behavior of $(TMTSF)_2ClO_4$ in high magnetic fields, derived from transport data. The FISDW diagram is reentrant, with the normal metal state occurring at both low and high field, and two values of H for the same T_c. This result is beyond and contra-

dictory to the expected behavior from present theories. The picture which emerges for $T \sim 0.5$ K is as follows: superconducting metal up to 0.03 T, "normal" metal to $\simeq 3.5$ T, six field-induced spin-density-wave semimetal phases with the Fermi level jumping between Landau-level gaps from 3.5 to 7.5 T, a new state with E_F changing to keep a constant Landau-level filling over the extraordinary range from 7.5 to 26 T, and reentrance of the normal state above 26 T.

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Note added.—After this manuscript was submitted we learned of recent work by Yakovenko.[20] This work treats the FISDW's theoretically with an entirely different perspective than Refs. 9–13 and predicts a reentrance of the normal phase at high field. Whether the present phase diagram is in agreement with this new model awaits further analysis and computation.

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