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Low-field and anomalous high-field Hall effect in $(\text{TMTSF})_2\text{ClO}_4$

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Résumé. — Nous présentons une étude de l'effet Hall effectuée à basse température dans $(\text{TMTSF})_2\text{ClO}_4$ après refroidissement lent, jusqu'à un champ de 80 kOe placé perpendiculairement au plan $(a-b)$. La très faible résistance de Hall dépendant linéairement du champ magnétique jusqu'à 40 kOe indique l'existence d'un conducteur à surface de Fermi quasi-planaire et une densité de porteurs correspondant à la stoechiométrie. La croissance très brutale de la constante de Hall observée en champ élevé correspondant à une transition vers un état semi-métallique. Les marches et plateaux de la résistance de Hall observés dans l'état semi-métallique au-dessous de 0,7 K suggèrent soit la quantification de la constante de Hall des porteurs bidimensionnels dans les plans $(a-b)$ soit l'existence d'une série de transitions du type instabilité électron-trou (phases excitoniques).

Abstract. — We report the study of the Hall effect, at low temperature, in $(\text{TMTSF})_2\text{ClO}_4$ (slow-cooled state), up to 80 kOe, with the field perpendicular to the $(a-b)$ plane. We show that the linear field dependence of the weak Hall resistance, up to 40 kOe, supports the interpretation of the conducting phase in terms of a quasi planar Fermi surface with a density of carriers corresponding to the stoichiometry of the salt. At higher field, a strong and sharp increase of the Hall constant, is the signature of a phase transition to a semi-metallic state. The transition magnetic field is very temperature dependent. Below 0.7 K, in the semi-metallic state, remarkable steps and plateaux of the Hall resistance are observed, suggesting either the quantization of the Hall constant of carriers in weakly coupled $(a-b)$ planes or the existence of a sequence of electron-hole instabilities (excitonic phases).

1. Introduction.

The organic conductor $(\text{TMTSF})_2\text{ClO}_4$ exhibits a variety of fascinating properties : a structural phase transition at 24 K [1], superconductivity at 1.2 K under ambient pressure [2], a spin density wave (SDW) ground state under magnetic field [3]. Moreover, the transverse magneto resistance of this conductor is large and anisotropic [4]. Oscillations of the magneto resistance are observed at high fields ; they have been attributed to Shubnikov-de Haas oscillations on a Fermi surface (FS) consisting of compensated tubes of electrons and holes [5, 6]. This two-dimensional (2D), semi-metallic FS is consistent with the low density of states determined from high field and low

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temperature specific heat measurements [7]. However this model is well established only for magnetic fields higher than a threshold field which is strongly temperature and orientation dependent. Moreover, the attribution of the oscillations to standard Shubnikov-de Haas effect (SdH) is not fully satisfying since :

- i) very small number of electrons and holes coexist with cyclotron masses of the order of unity [8];
- ii) the oscillations are pretty sharp and do not resemble standard quantum oscillations [8];
- iii) there is no well established periodicity of the oscillations in $1/H$ [9, 10];
- iv) the oscillation fields are strongly temperature dependent [9, 10];
- v) temperature dependent magnetic field hysteresis of the high field oscillation has been reported [9].

The existence of the threshold field is a very specific feature which has received several conflicting interpretations :

- i) the transition from a zero magnetic field optimal nesting vector of the FS to a different nesting vector becoming optimal under high magnetic field [5];
- ii) a cross-over from a three-dimensional to a quasi-two-dimensional behaviour of the Fermi surface topology when the Landau splitting ($\hbar\omega_c$) becomes larger than t_{\perp}^2 the overlap integral along the weak coupling direction [6];
- iii) the transition from a quasi-1D to a quasi-2D FS; this topology change being connected to a field-induced phase transition from a non magnetic metal to a magnetic semi-metal [3, 11].

We report here Hall voltage measurements providing new informations about the nature of both the high conducting state of $(\text{TMTSF})_2\text{ClO}_4$ and its semi-metallic high field state.

2. Experimental details.

Three samples have been studied and provided similar qualitative results. The results shown and discussed here were obtained with a crystal of $(a \times b^* \times c^*) = (2.2 \times 0.3 \times 0.18) \text{ mm}^3$. The magnetic field is aligned, within less than 10° , along the c^* direction. The current flows along the highly conducting a -axis while the Hall voltage develops along the b^* -axis. The electrical leads are $17 \mu\text{m}$ diameter gold wires glued on to gold evaporated contacts with silver paint. The width of the Hall voltage contacts is less than 0.2 mm and the shortest distance to an injection contact is 0.7 mm .

The measurements are performed using an A.C. technique with a current up to $100 \mu\text{A}$ at 77 Hz . Below 2 K , within a day, the reliability of the temperature regulation is better than 1 mK .

The transverse magneto resistance is particularly large in our geometry; in order to avoid spurious effects, at a regulated temperature, we have defined the Hall voltage (V_H) as half the difference between the measured transverse voltage with upwards and downwards magnetic fields. In both cases the magnetic field is swept with similar speed and range of variation.

The Hall coefficient R_H is given by the formula $R_H = (V_H/IH) \times W$ where W is the width in the c^* -direction (0.18 mm in the discussed results).

The crystals are cooled down from 30 K to 4.2 K in more than 3 hours and therefore must be considered as perfectly relaxed [12]. We have checked that in zero field the transition to the superconducting state is observed at 1.2 K .

3. Experimental results.

Down to 0.1 K , the Hall voltage is linear *versus* magnetic field up to 30 kOe (Fig. 1). The Hall coefficient calculated from this variation is $R_H = 4 \times 10^{-9} \text{ m}^3/\text{A.s}$ at 0.5 K . At 0.1 K and 1 K

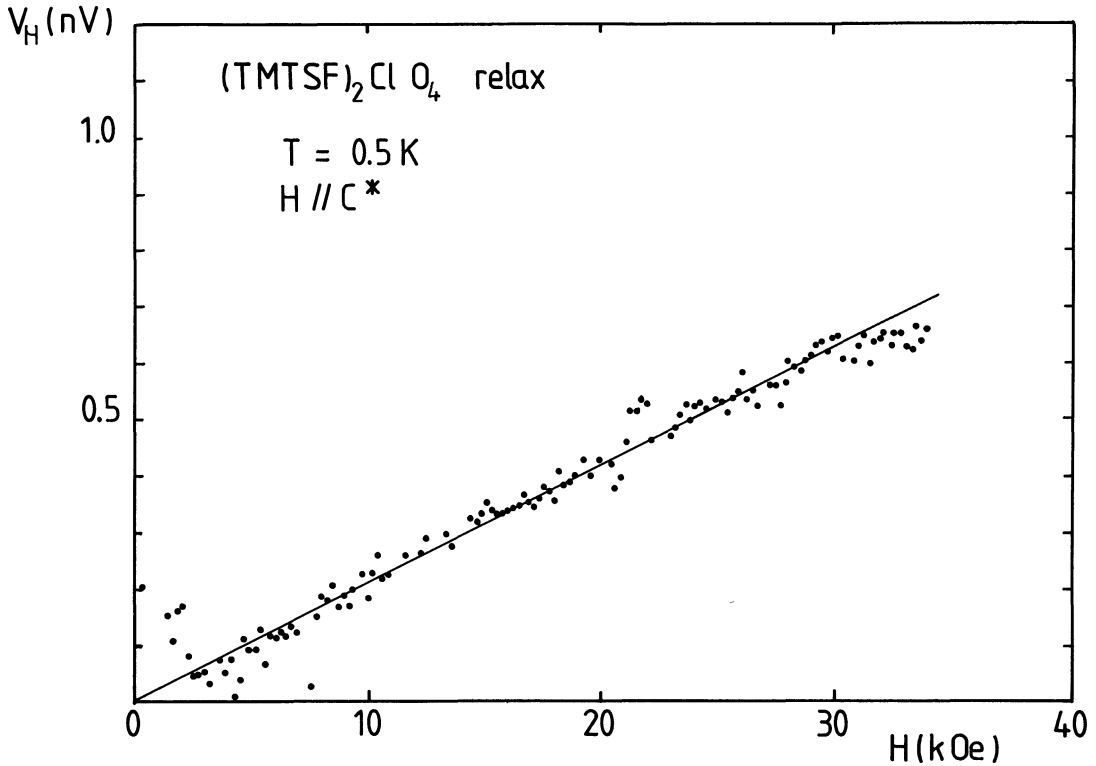


Fig. 1. — The low magnetic field Hall voltage.

the calculated R_H values are within 10% of the 0.5 K value. The low magnetic field Hall voltage is small: at 0.5 K, in 30 kOe, the Hall voltage is less than 1.5% of the measured transverse voltage. Above 2 K the reliability of the temperature regulation was not sufficient to allow quantitative determination of V_H but we can claim that no significant qualitative modification appears at least up to 4.2 K.

Above 30 kOe, the Hall voltage behaviour is not so simple and at a magnetic field which is strongly temperature dependent it changes sign and increases strongly. At 1.3 K (Fig. 2a) these features occur in the 61-65 kOe field range. It is also in the very same field range that onset of Shubnikov-de Haas oscillations [5] transition to a low density of states system [7] and transition to a SDW state have been observed [3]. At lower temperature the situation is much more complicated; at 0.1 K (Fig. 2b) V_H changes sign below 40 kOe and after a 40-50 kOe bump increases sharply in two steps at 51 and 62 kOe (the 51 kOe step exhibiting a weak shoulder at 54 kOe).

Between 57 and 61 kOe on the one hand and 64 and 80 kOe on the other hand, the Hall voltage is only very weakly field dependent. At 70 kOe, the ratio between the extrapolated low-field Hall voltage and the high-field Hall voltage is more than 250. Between 1.3 and 0.1 K an increase of the amplitude of the Hall voltage on both sides of the step at 60 kOe is observed on cooling together with a very slight shift of the position of the steps towards lower fields. In figure 3 is shown the temperature variation of both the high-field and low-field V_H of the high-field step: V_H on the low-field side does not saturate at low temperature whereas it does on the high-field side below about 0.2 K.

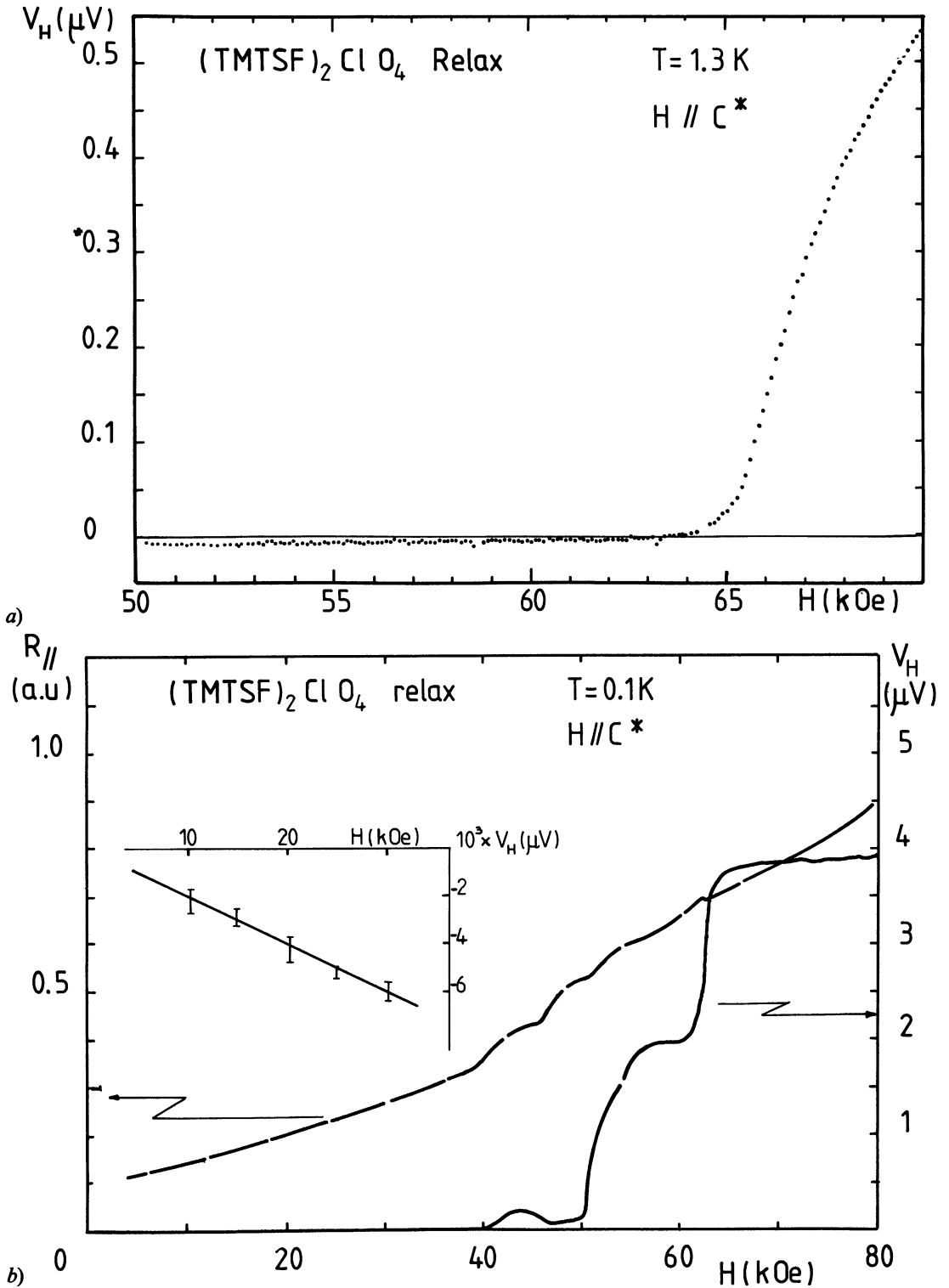


Fig. 2. — The high magnetic field Hall voltage : a) at 1.3 K, b) at 0.1 K. The insert shows the low magnetic field part of this variation. The transverse magneto resistance is also displayed. The measuring current is 100 μA .

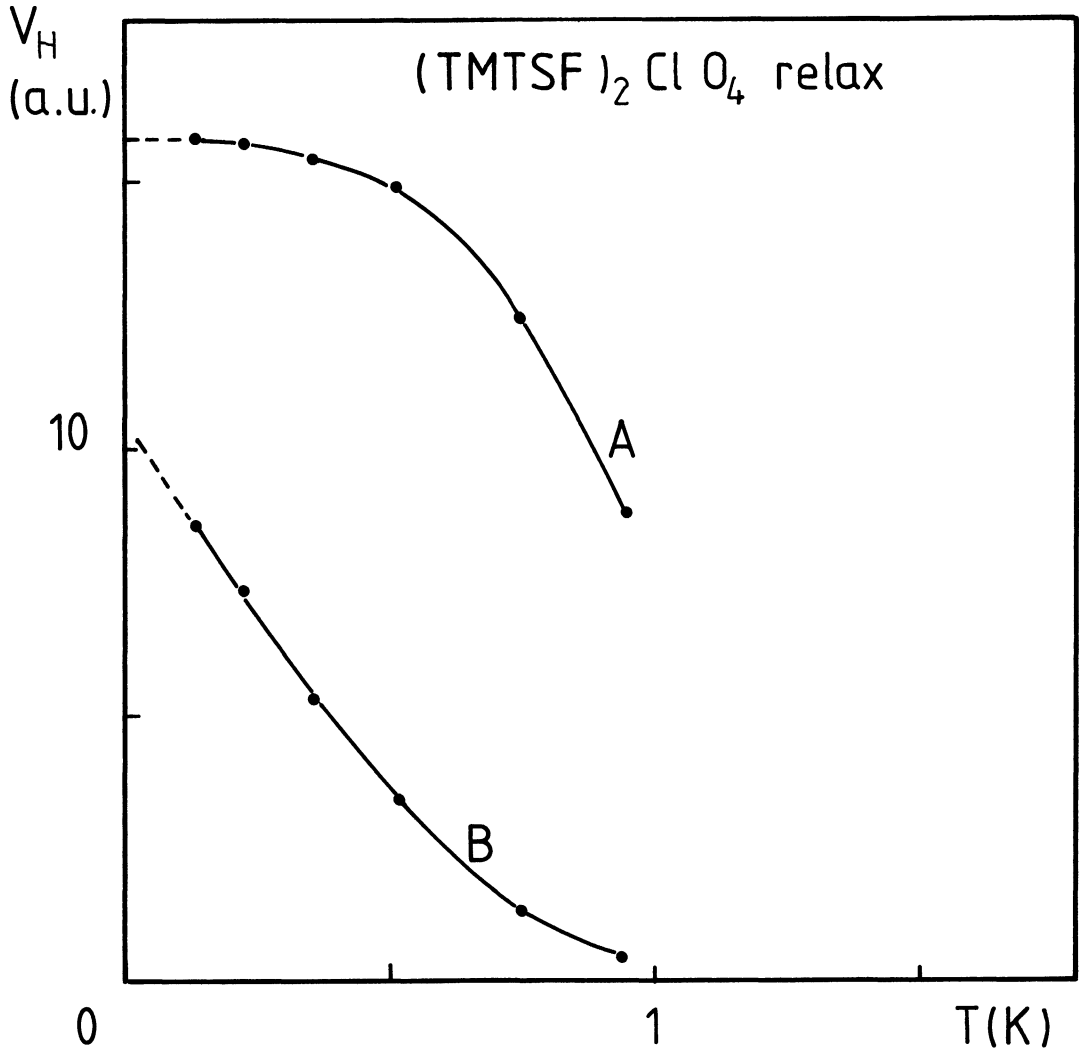


Fig. 3. — The Hall voltage amplitude on the high-field side (A) and the low-field side (B) of the 60 kOe step.

4. Discussion.

The low magnetic field Hall coefficient $R_H = 4 \times 10^{-9} \text{ m}^3/\text{A} \cdot \text{s}$ is small, about 5×10^{-4} smaller than the Hall voltage observed in the semiconducting (SDW) state of $(\text{TMTSF})_2\text{PF}_6$ at 4.2 K [13]. This low value compares well with the room temperature value of the Hall constant of TTF-TCNQ [14], HMTSF-TCNQ [15] or TMTSF-DMTCNQ [16]. In the model developed by Kwak [5] at low temperature, in low magnetic fields, $(\text{TMTSF})_2\text{ClO}_4$ is a perfectly compensated 2D semimetal, the FS involves only 10^{-4} of the Brillouin zone. To obtain a value of R_H of the order of the measured one, we need a nearly perfect compensation of the effect of the two types of carriers. A 10^{-4} compensation for R_H implies a $\approx 10^{-2}$ compensation for the mobilities and owing to the very different shape of electron and hole FS this seems unlikely. We now consider a quasi-one-dimensional FS; the standard expression for the low-field Hall coefficient, in an anisotropic tight binding model [14] is $R_H = (1/nec) \times (k_F a / \text{tg } k_F a)$ where a is the distance between organic

molecules in the high conductivity direction, $k_F = 3\pi/4 a$ (the weak dimerization of the TMTSF molecules in the organic stack does not modify the energy band near k_F). This gives $R_H = 3.4 \times 10^{-9} \text{ m}^3/\text{A} \cdot \text{s}$. The nearly perfect agreement between calculated and measured values should not be taken too seriously but it is a proof that we need a large number of carriers. In the model proposed by Chaikin *et al.* [6] the threshold field manifests itself as a transition from a 3D to a 2D Fermi surface when the coupling along c becomes smaller than the energy difference $\hbar\omega_c$ between Landau levels. As t_{\perp}^c amounts to $\approx 1 \text{ meV}$ (11 K) the condition $\hbar\omega_c > t_{\perp}^c$ is satisfied above 70 kOe for electrons with free-electron masses. However, Chaikin's suggestion takes care neither of the rapid increase of the Hall constant in the high-field regime nor of the occurrence of magnetism.

The low field Hall data establish the quasi 1D nature of the Fermi surface. Therefore the large Hall voltage anomalies developing at the threshold field must be considered as instabilities in a Q-1D electron gas. On account of the strong coupling along the b -direction the 2D character of the transport properties in the $(a-b)$ plane is very pronounced in the $(\text{TMTSF})_2\text{X}$ series. The electron motion becomes coherent at low temperature even along the transverse b -direction according to the observation of a transverse plasma edge at IR frequencies [17]. The transverse plasma edge does not necessarily imply closed orbits (for example in the Q-1D regime of the Fermi surface) but closed orbits are likely to exist in high-field semi-metallic regime. The high-field Fermi surface consists probably of small cross-section warped tubes parallel to the c^* -direction. As far as the anomalous high-field Hall voltage behaviour is concerned we wish to suggest and discuss briefly two possible interpretations. First, a crystal of $(\text{TMTSF})_2\text{X}$ may be considered as a packing of conducting $(a-b)$ planes along the c -direction. In the high-field semi-metallic regime electron or hole orbits are closed in the $(a-b)$ plane but probably rather anisotropic [18]. Moreover at high-fields, when $\hbar\omega_c > t_{\perp}^c$ their cross-sectional area will not vary significantly along the k_c direction. Thus the carriers in the $(a-b)$ planes behave as a system of two-dimensional carriers. A $(\text{TMTSF})_2\text{X}$ crystal is then indeed a multilayer structure comprising a large number of identical 2D electron layers electrically connected in parallel by the Hall probes.

This is a situation where the Hall voltage adopts a quantized behaviour *versus* magnetic field instead of the usual linear relationship [19, 20] : the Hall resistance ρ_{xy} becomes $h/e^2 i$ where h and e are respectively the Planck constant and the electron charge, and i is the number of filled Landau levels. It is certainly tempting to establish the connection between the Hall voltage steps observed at high-field and the quantization of the Hall resistance in a multilayered 2D electron gas. Order of magnitude wise this comparison makes sense. A crystal which is $180 \mu\text{m}$ thick along the c -direction contains about 1.5×10^5 $(a-b)$ layers. The measuring current per layer becomes therefore $\approx 0.6 \times 10^{-9} \text{ A}$ for a total current of $100 \mu\text{A}$ and leads to a Hall resistance plateau $\rho_{xy} \approx 6 \text{ k}\Omega$ above 63 kOe (Fig. 2b). The latter value of the Hall resistance is admittedly very close to the quantized value of the Hall resistance for $i = 4$ ($h/4e^2 = 6453 \Omega$).

According to the data of figure 3 the value of the plateau labelled B is strongly temperature dependent. However the ratio between B and A Hall resistance values extrapolates to $3/2$ at zero temperature. This feature suggests that in terms of Hall quantization the B-plateau could be related to 6 filled Landau levels below the Fermi level. In this picture steps are expected above 100 kOe and below 45 kOe : the step at $\approx 50 \text{ kOe}$ (Fig. 2b) occurs at too high a value of the magnetic field for Hall quantization. However it is likely that a large fraction of the B-plateau is removed at low-fields by the existence of the 2D to 1D phase transition. The sheet carrier density derived from the data in figure 2b leads to $\approx 7.3 \times 10^{11} \text{ cm}^{-2}$. This value of the carrier density is in fair agreement with the data obtained in heterostructures [20], for which quantum effects are observed in the same field regime.

The considerable temperature dependence of the B-plateau cannot be readily understood in terms of quantized Hall resistance (which should not vary with temperature in simple 2D geo-

metries). However it may be attributed to some possible temperature dependence of the Fermi surface in the high-field state. Another serious problem in this model is the diagonal resistance which does not vanish in the Hall plateau regions but shows only a very weak peak related to the step of Hall resistance (see Fig. 2b at 63 kOe).

An alternative interpretation is that the anomalous properties of the Hall effect in high-field are associated with a succession of phase transitions (Fig. 4). Sequences of electron-hole instabilities have been proposed for small gap (overlap) semiconductors (semi-metals) [21]. The different phases differ from each other by having different order parameters. Then in this picture the field temperature diagram (Fig. 4) would be interpreted as a phase diagram. It displays a low-field non-magnetic state and several SDW states above the onset field. The phase transition at the onset field is likely to be second order since the order parameter (SDW amplitude) reaches a zero value at the onset field [3]; hence no hysteresis is observed at the magnetic-non-magnetic transition. However, the transitions between various SDW states could be first order (the SDW

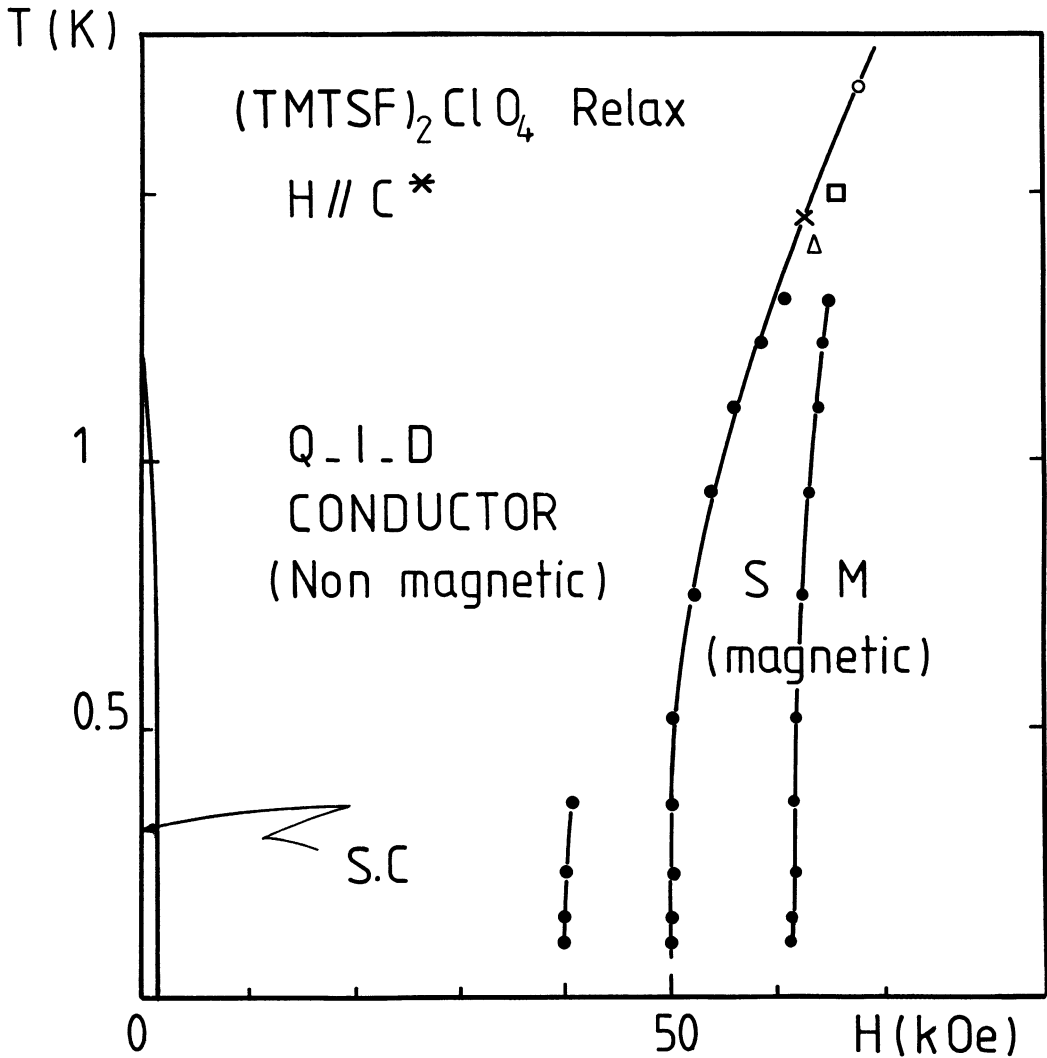


Fig. 4. — Possible phase diagram of $(\text{TMTSF})_2\text{ClO}_4$ with the magnetic field aligned along c^* . \bullet Hall voltage anomalies, \times phase transition detected by specific heat measurements [7], Δ , \square phase transition detected by NMR; respectively ^{77}Se NMR [3] and ^1H NMR [22].

amplitude or orientation jumping discontinuously from one value to another). We wish to mention that the phase diagram of $(\text{TMTSF})_2\text{ClO}_4$ presents many features in agreement with the model of nested excitonic phases [21]. Starting from the conducting phase, the first transition is an Overhauser-like instability to a magnetic semi-metallic state. Subsequent phases are also magnetic with successive drops of the density of carriers at increasing magnetic fields. In each SDW phase the gap occurring on the nested regions of the Fermi surface (proportional to the SDW amplitude) increases with the magnetic field. Consequently, the small overlap between hole and electron bands decreases for increasing fields with a concomitant decrease in the density of carriers. However the quasi independence of the Hall resistance on temperature and magnetic field in the plateau region cannot be readily explained by successive changes in the Fermi surface.

In conclusion, we have reported the first measurement of the Hall constant in the conducting state of $(\text{TMTSF})_2\text{ClO}_4$ at low temperature. The data indicate conclusively the existence of a phase transition between a low-field Q-1D Fermi surface conductor and a high-field semi-metallic regime. The high-field Hall constant displays very striking steps which may be associated either with Hall quantization in a 2D electron gas or with the existence of a sequence of electron-hole instabilities (excitonic phases). Furthermore, the rather complex structure of $(\text{TMTSF})_2\text{X}$ conductors and the magnetic character of the 2D Fermi surface phase may complicate significantly the interpretation. Finally, since at the highest magnetic fields $\hbar\omega_c \gg kT$, it is possible that there is a mixing between 2D quantization and excitonic instabilities in $(\text{TMTSF})_2\text{ClO}_4$. We believe that these interpretations are the most promising ones on which to base further studies.

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