Magnetoresistance of the organic superconductor bis-tetramethyltetraselenafulvalenium perchlorate [$(TMTSF)_2ClO_4$]: Kohler's rule

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We report a study of the magnetoresistance of the organic superconductor bis-tetramethyltetraselenafulvalenium perchlorate [$(TMTSF)_2ClO_4$] from 1.8 to 20 K in fields up to 79 kG, for current flow both parallel and perpendicular ($\vec{c}^*$) to the highly conducting $\vec{a}$ axis. For the latter, Kohler's rule is obeyed and the results can be understood in terms of standard theory for an open Fermi surface. We argue that $\vec{a}$ is not exactly a principal axis of the conductivity tensor. Then the field dependence of the longitudinal conductivity can be understood within the same picture. For slowly cooled samples there are deviations from Kohler's rule which can be attributed to magnetic breakdown of superlattice gaps.

There is currently much interest in novel conduction mechanisms in quasi-one-dimensional conductors.[1] One fundamental question in this field is whether the electrical conductivity of these unusual materials can ever be understood in terms of the Boltzmann-equation approach developed for the usual three-dimensional metals.[2–4] A consequence of the latter is that the magnetoresistance obeys Kohler's rule (KR), which states that the increase in resistivity in a magnetic field H, relative to the zero-field value ρ_0, is a universal function of H/ρ_0,

$$\Delta\rho/\rho_0 = f(H/\rho_0) \ , \tag{1}$$

at all temperatures T and fields H.

Although the magnetoresistance of linear chain conductors is often large,[1] there have been few attempts to see whether KR applies to this class of material, and as far as we know, until now no evidence for its validity was discovered.[5]

The organic conductor bis-tetramethyltetraselenafulvalenium perchlorate $(TMTSF)_2ClO_4$ shows metallic $\rho(T)$ behavior and becomes superconducting at 1.2 K.[6] Recently it was shown that slowly cooled, relaxed (R) samples undergo a phase transition at 25 K,[7] where the lattice period doubles along $\vec{b}$ (Ref. 8) due to ordering of the noncentrosymmetric ClO_4^- anions. Rapidly quenched (Q) samples do not show this ordering; they form a spin-density-wave state below 4.2 K,[7,9] and superconductivity is suppressed.[10] Recent band-structure calculations[11] indicate that the Fermi surface (FS) remains open in R samples at all T and in Q samples above 4.2 K. There is experimental support for this from, for example, measurements of susceptibility anisotropy.[12]

In this work we report a study of magnetoresistance for current flow parallel ($\rho_\parallel$) and perpendicular ($\rho_\perp$) to the conducting chains for both R and Q samples. We pay especial attention to KR and to what extent our results can be understood in terms of classical magnetotransport concepts and the proposed FS.[11] Other related studies of $(TMTSF)_2ClO_4$ have focused on $\rho_\parallel$ (Ref. 5) and more on its high-field behavior.[13–16] Also they have not made such a detailed comparison with FS theory at low fields.

Conventional experimental techniques were used, four electrical contacts being made to the crystals with silver paste. Crystal dimensions were typically $5\times0.5\times0.3$ mm^3 for $\rho_\parallel$, while for $\rho_\perp$ they were cut to approximately 0.3 mm along the $\vec{a}$ axis. Their orientation was subsequently checked by x-ray diffraction. For the $\rho_\perp$ samples this showed that the current contacts were along the (011) direction. Taking the known anisotropy,[1] the sample dimensions, and the shape of the equivalent isotropic sample[17] into account we conclude that our measured values of $\rho_\perp$ correspond to ρ_{c^*}. This is confirmed by the high room-temperature value 5 Ω cm and the agreement between our $\rho_\perp(T)$ data in Fig. 1 and independent measurements of $\rho_{c^*}(T)$.[18]

Measuring currents of 10^{-4} and 10^{-5} A were used for $\rho_\parallel$ and $\rho_\perp$ samples, respectively; they had room-temperature resistances of about 1 and 200 Ω with resistance ratios in the range 100–400. The results given here refer to the orientation at which $\Delta\rho/\rho$ was a maximum at 70 kG and 4.2 K, i.e., approximately $\vec{H}\parallel\vec{c}^*$ for $\rho_\parallel$ and $\vec{H}\parallel\vec{b}^*$ for $\rho_\perp$. The Q state was obtained by allowing the sample to cool rapidly (30 s) from 40 to 10 K. Because of annealing processes,[7] measurements on Q samples were restricted to 12 K or below.

Figure 1 shows the overall T dependence of $\rho_\parallel$ and $\rho_\perp$ obtained in these experiments for both R and Q states. The phase transition at 25 K is even more clearly visible in $\rho_\perp$ of R samples than it was in $\rho_\parallel(T)$,[18,19] and there is evidence for a second small anomaly near 4.2 K. Corresponding data for $\rho_\parallel(T)$ are shown in the lower part of Fig. 1. In the region where there are no sharp jumps in resistance due to microcracks (down to 180 K) a good T^2 law is obeyed. Below 20 K $\rho_\parallel$ approximately follows the law $A+BT^2$.

Figure 2 shows the magnetoresistance data for $\rho_\perp$ in the form of Kohler plots. The upper plot shows the most surprising and striking result of the present work. We find that for R samples $\rho_\perp$ (ρ_{c^*}) follows KR over a wide range of fields and temperatures, 1.8 to 22 K and up to 78 kG for $\Delta\rho/\rho$ values up to 60. There is an H^2 dependence up to $\Delta\rho/\rho=4$. The right-hand part of Fig. 2 shows Kohler plots for Q samples; the results for the R state are represented by

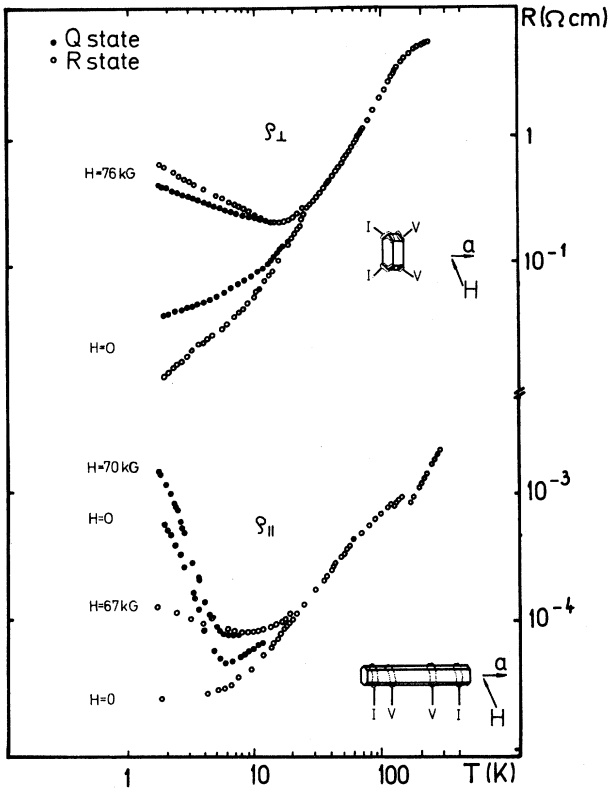

FIG. 1. Overall view of magnetoresistance results for $(TMTSF)_2ClO_4$. Sketches of contact geometry are also shown.

the dashed line. It can be seen that the results for Q and R samples overlap above about 5 K. Below 5 K Q samples show increasing deviations from KR. This is qualitatively what is to be expected for a spin-density-wave state in Q samples below 5 K.[9,20]

In contrast to Fig. 2, Fig. 3 shows that KR is not obeyed for R samples when current flows along the $\vec{a}$ axis. But in fixed fields a type of KR *is* obeyed in that $\Delta\rho/\rho_0$ is proportional to ρ_0^{-2} up to 20 K. This law is also obeyed by independent data.[5] The deviation at 78 kG and 2 K is probably due to the threshold field,[15] which is believed to mark a transition to a spin-density-wave state.[9,21] Above 5.5 K the Q sample *does* obey KR, and there is also a tendency for R samples to approach the Kohler line of Q samples at fields of approximately 70 kG and also as T is increased above about 12 K. These points will be explained below in terms of standard theory[2,3] for the conductivity tensor σ of three-dimensional metals.

The FS is described by the energy dispersion law[11]

$$\epsilon = -2t_{\parallel}\cos\vec{k}\cdot\vec{a} - 2t_1^b\cos\vec{k}\cdot\vec{b} - 2t_1^c\cos\vec{k}\cdot\vec{c} \ ,$$

with $t_{\parallel} \sim 10t_1^b \sim 100t_1^c$. We approximated the actual triclinic structure[22] by a similar monoclinic one with $\vec{a} < \vec{b} = 70°$ and $a = 3.63$ Å. For $\vec{H} \parallel \vec{c}^*$, the leading terms in the low-field limit have the form

$$\sigma_{aa}(H) = \sigma_{aa}(0)(1-\omega_b^2\tau^2) \ ,$$

$$\sigma_{b^*b^*}(H) = \sigma_{b^*b^*}(0)(1-\Omega_b^2\tau^2) \ ,$$

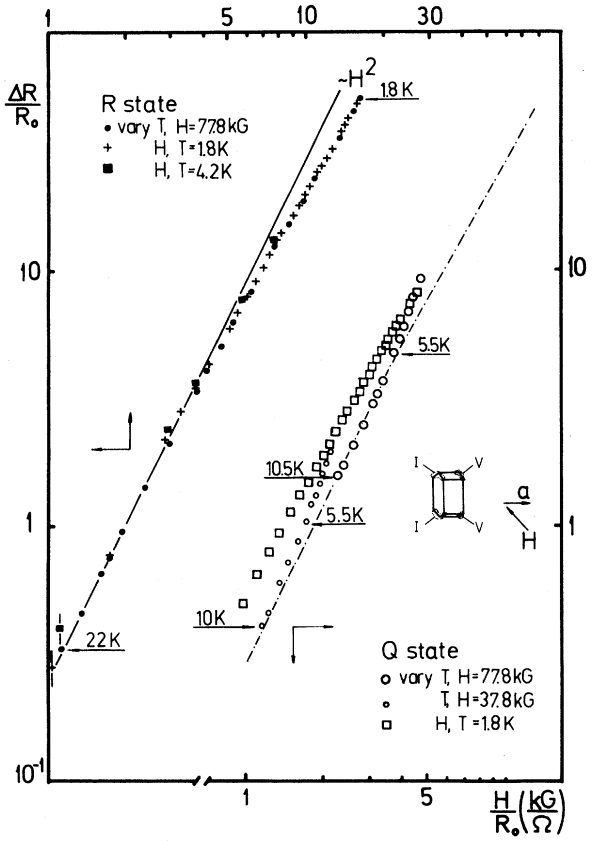

FIG. 2. Kohler plots of the transverse resistivity of $(TMTSF)_2ClO_4$.

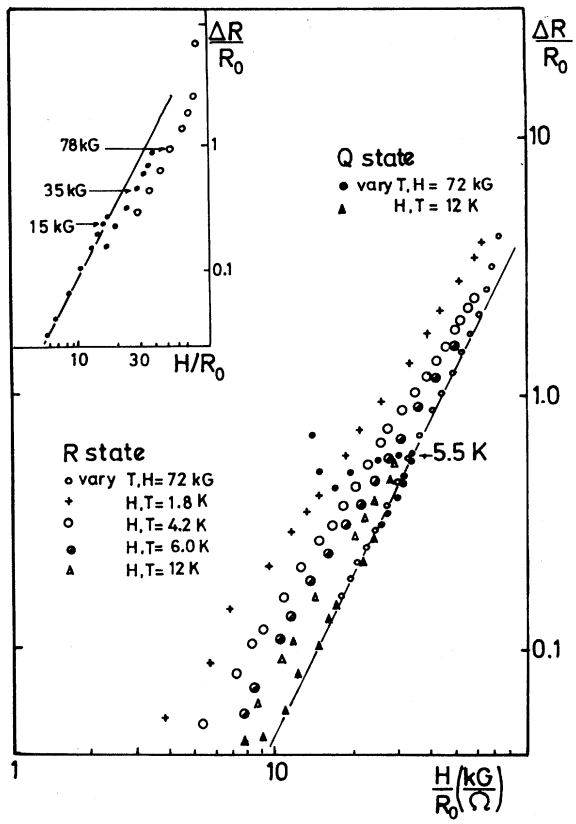

FIG. 3. Kohler plots for the parallel resistivity of $(TMTSF)_2ClO_4$; the lines of slope 2 correspond to a $1/\rho_0^2$ law at fixed H.

and

$$\sigma_{ab^*}(H)=\sigma_{ab^*}(0)+\sigma_{aa}(0)\sigma_{b^*b^*}(0)R_H H \ .$$

In these formulas the larger cyclotron frequency $\Omega_b = eb\cos 20 v_a H/\hbar c'$, where e is the electronic charge, $\hbar$ is Planck's constant, c' is the velocity of light, and v_a is the Fermi velcoity along $\vec{a}$, $\omega_b \simeq \Omega_b t_\perp^b/t_\parallel$, τ is the relaxation time, and R_H the low-field Hall constant. All other components of σ are equal to their zero-field values. For $\vec{H}\parallel\vec{b}^*$, similar formulas apply, but with $b(b^*)$ and $c(c^*)$ interchanged, the cos20 factor omitted, and $\sigma_{ac^*}(0)=0$. At high fields $\sigma_{b^*b^*}$ does not saturate but goes as $1/(1+\Omega_b^2\tau^2)$.

As usual the magnetoresistance must be determined by inverting $\sigma(H)$ while taking account of the sample geometry.[23] With use of the formula for R_H,[24] it transpires that our measured values of $\rho_\perp(H)$, along (011), are dominated by $1/\sigma_{c^*c^*}$. The above equations will thus account for the field dependence of $\Delta\rho_\perp/\rho_\perp$, its magnitude, and KR, provided that $\Omega_c\tau=1$ for R samples at 10 kG and 2 K. This in turn requires that $v_a\tau$ is $1400a$, i.e., 700 times its room-temperature value. Such a value corresponds well to the resistance ratios observed for both $\rho_\parallel$ and $\rho_\perp$.[18,19] Therefore we conclude that at low T and H electron transport along $\vec{c}^*$ *can* be understood within the classical coherent three-dimensional picture, which is not widely appreciated, but has been suggested recently[15] on other grounds.

In view of the recent controversy[1,25] regarding a superconducting fluctuation contribution to the conductivity, it is important to see whether our results for $\rho_\parallel(H)$ can be understood in the same way. At first sight they cannot because $t_\parallel^2/(t_\perp^b)^2$ is about 300,[11] and thus the above equations give $\Delta\rho_\parallel/\rho_\parallel$ a factor $300c^2/b^2=900$ smaller than $\Delta\rho_\perp/\rho_\perp$ for the same τ. Experimentally this ratio is about 25 for Q samples above 6 K , and for R samples it falls from 25 to 4 as H is reduced from 70 to 10 kG. However, a crucial point is that due to the low symmetry $\sigma_{ab}^*(0)$ is not zero. When the conductivity tensor is inverted to obtain $\Delta\rho_\parallel/\rho_\parallel$, the latter contains a $\sigma_{b^*b^*}(H)$ term. We find that this term goes as $(\bar{v}_{b^*})^2\Omega^2\tau^2/\overline{v_{b^*}^2}$, where v_{b^*} is the b^* component of the Fermi velocity and the average is over the positive sheet(s), $k_a>0$, of the FS. By itself the above dispersion formula gives too small a value of $\bar{v}_{b^*}$ to account for Fig. 3. However, if one takes into account the usual condition that the FS intersects the zone boundary at right angles, larger values of $\bar{v}_{b^*}$ are obtained, and they can easily be high enough to give $\Delta\rho_\parallel/\rho_\parallel \sim \Omega_b^2\tau^2/10$, in agreement with experiment. Thus the magnetoresistance in the Q state and the KR behavior are understood nearly as well as for $\rho_\perp$.

In the R state the doubling of the b lattice parameter increases Ω_b by a factor of $2b/\cos 20$. If the gaps introduced by the superlattice are small compared with $t_\perp^b$, then $\bar{v}_{b^*}$ averaged over both FS sheets,[11] and hence $\sigma_{ab^*}(0)$ will not be altered. Thus the R samples should have 4.5 times larger $\Delta\rho_\parallel/\rho_\parallel$ than Q samples at constant τ. As shown in Fig. 3, this is approximately the case at the lowest fields. However KR is not obeyed for R samples as it should be in terms of the above picture. We propose that this is due to magnetic breakdown[4,26] across the superlattice gap. As H is increased above a few kilogauss, magnetic breakdown becomes progressively more important, leading to deviations from KR. At high fields, ~ 70 kG, the influence of the superlattice gap is negligible and this is why the results for R and Q samples overlap on Kohler plots, as shown in Fig. 3. If the superlattice gap is large compared with kT and T independent, then at a fixed field the measured magnetoresistance will be a certain constant combination of the Q and low-field R values. Thus it should go as τ^2 or $1/\rho_0^2$, as is observed experimentally, Fig. 3. Note that the measurements of $\rho_\perp$, which are dominated by $1/\sigma_{c^*c^*}(H)$, will not be affected by magnetic breakdown, because in this case we had $\vec{H}\parallel\vec{b}^*$, and this is why KR is obeyed for $\rho_\perp$ of both R and Q samples.

In our case, the usual condition for breakdown[4] becomes, for $\vec{H}\parallel\vec{c}^*$, and an energy gap E_g along $\vec{b}^*$ $(\hbar\Omega_b t_\parallel)^{1/2} > E_g$. With Ω_b given as above, taking $2b$ rather than b, we find that a field of 70 kG will cause breakdown across a gap $E_g = 9.4\times 10^{-2} t_\parallel \sim 300$ K. This is of the required order of magnitude, namely, $kT < E_g \lesssim t_\perp^b$, for the whole discussion given here to be self-consistent. Magnetic breakdown could also play an important role in inducing the transition to a magnetic state[9,21] in R samples at about 80 kG, because in the absence of superlattice gaps the FS nesting wave vector has been shown[11] to be nearer commensurability with the lattice. However more theoretical work is needed to see whether the above formula does indeed describe breakdown between two different types of open orbits because it is usually applied in situations where the high-field orbits are free-electron-like.

In summary we believe that most of the magnetoresistance measurements reported here for single crystals of $(TMTSF)_2ClO_4$ at temperatures between 1.8 and 22 K and fields up to 78 kG can be understood in terms of classical theory[3] for an open Fermi surface in the relaxation-time approximation. For current flow perpendicular to the conducting chains (c^*), the magnetoresistance is relatively straightforward provided the electron mean free path *along* the chains is as high as 1500 lattice constants at 2 K. There are complications for current flow along the chains; in our picture, the magnetoresistance is only large because of the low crystal symmetry. Furthermore, in the relaxed state there are deviations from Kohler's rule which may be due to magnetic breakdown.

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