Magnetoresistance and magnetic breakdown in the quasi-two-dimensional conductors $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4[M=\mathrm{K,Rb,Tl}]$

Ross H. McKenzie*
School of Physics, University of New South Wales, Sydney 2052, Australia

G. J. Athas
Physics Department, Boston University, Boston, MA 02215

J. S. Brooks
National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306

R. G. Clark, A. S. Dzurak, R. Newbury, R. P. Starrett, and A. Skougarevsky
School of Physics and National Pulsed Magnet Laboratory, University of New South Wales, Sydney 2052, Australia

M. Tokumoto, N. Kinoshita, T. Kinoshita, and Y. Tanaka
Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan

(Received 21 June 1996)

The magnetic-field dependence of the resistance of $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4[M=\mathrm{K,Rb,Tl}]$ in the density-wave phase is explained in terms of a simple model involving magnetic breakdown and a reconstructed Fermi surface. The theory is compared to measurements in pulsed magnetic fields up to 51 T. The value implied for the scattering time is consistent with independent determinations. The energy gap associated with the density-wave phase is deduced from the magnetic breakdown field. Our results have important implications for the phase diagram. [S0163-1829(96)52036-9]

Conducting organic molecular crystals based on the bis-(ethylenedithio tetrathiafulvalene) (BEDT-TTF) and tetramethyltetraselenafulvalene (TMTSF) molecules are interesting low-dimensional electronic systems.[1,2] The family $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4[M=\mathrm{K,Rb,Tl,NH}_4]$ is of particular interest because such compounds have a rich phase diagram and coexisting quasi-one-dimensional and quasi-two-dimensional Fermi surfaces. Metallic, superconducting, and density-wave phases are possible, depending on temperature, pressure, magnetic field, and anion type.[2] At ambient pressure, the family with $M=$ K,Rb,Tl undergoes a transition from a metal to a density-wave (DW) phase at a temperature $T_{\mathrm{DW}}=$ 8, 9, and 12 K, respectively. There is currently controversy as to whether this is a spin-density wave or a charge-density wave.[3–6] This phase is destroyed above a magnetic field H_k known as the kink field (for $M=$K,Tl, and Rb, $H_k=$ 23, 27, and 32 T, respectively).[2,7]

The purpose of this paper is to present new measurements of the field dependence of the magnetoresistance up to 51 T and explain this dependence in terms of *magnetic breakdown* and a reconstructed Fermi surface in the DW phase. The field dependence has the following features (compare with Fig. 1). (i) At low fields the resistance increases rapidly up to $H_{\max}\sim$ 15 T. The maximum resistance is roughly an order of magnitude larger than the zero-field resistance. (ii) The resistance then decreases with increasing field. (iii) Above about 30 T the background (nonoscillating) resistance saturates to a value much larger than the zero-field resistance. (iv) At low temperatures hysteresis is seen near the kink field. This is because destruction of the DW phase is a first-order transition at low temperatures. (v) The maximum resistance increases and $H_{\max}$ decreases as the temperature is lowered. Measurements on poorer-quality samples give smaller maximum resistance.[8,9] (vi) As the angle between the field and the conducting planes is increased $H_{\max}$ increases[5,10–12] but H_k does not vary.[5,11]

The measurements shown in Fig. 1 were made at the Australian National Pulsed Magnet Laboratory.[13] Samples were studied in a top loading ^{3}He refrigerator and aligned so the magnetic field was in the least-conducting direction (the **b** axis). The voltage and current were also along the **b** axis. The magnet system was pulsed up to 51 T with a duration of 20 ms. Measurements were made with dc constant current (80–200 μA) sources and low noise, differential preamplifiers. Pick-up from the *dB/dt* term was never more than 50% of the signal above 25 T. The pick-up term was eliminated from the data by averaging forward and reverse current traces. A RuO_2 thermometer mounted within 5 mm of the sample was used to monitor the temperature before and after each pulse. No systematic changes in temperature were observed as a result of the pulse. Preliminary data for a single temperature was briefly reported elsewhere.[14,15] Similar results have been obtained by other groups on the K and Tl salts in fields up to 30 T[8–10,16,17] and on K up to 50 T.[18]

The room-temperature Fermi surface of $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4[M=\mathrm{K,Rb,Tl}]$ in the conducting plane, calculated within a tight binding model[19] is shown in the inset of Fig. 2. There is a cylindrical or quasi-two-dimensional hole Fermi surface and a quasi-one-dimensional electron Fermi surface consisting of two warped sheets. It is believed that the nesting of the quasi-one-dimensional Fermi

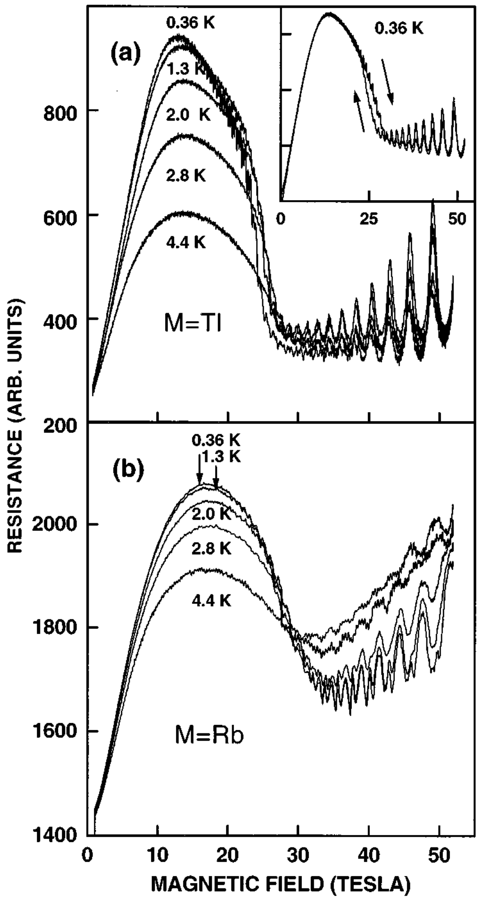

FIG. 1. Magnetic-field dependence of the resistance of $(\text{BEDT-TTF})_2M\text{Hg(SCN)}_4$ at different temperatures for (a) $M=\text{Tl}$ and (b) $M=\text{Rb}$. The pulsed magnetic field and the current direction were parallel to the least-conducting direction. Note that the resistance increases rapidly up to about 15 T, then decreases until about 30 T. The inset of (a) shows two curves corresponding to up and down sweeps of the magnetic field. They do not coincide near 27 T (the ''kink field'') due to hysteresis associated with the first-order transition there. For clarity only down sweeps are shown in the main figure. The measurements on Tl were four terminal and those on Rb were two terminal with a large contact resistance.

urface is responsible for the formation of the DW phase. The DW introduces a new periodic potential with wave vector **Q** into the system resulting in reconstruction of the quasi-two-dimensional Fermi surface. Two different reconstructions of the Fermi surface have been proposed[20,21] and are described below. We shall focus on the one shown in Fig. 2, *purely for reasons of calculational simplicity.* We show here that if magnetic breakdown, which causes the holes to return to their original unreconstructed closed orbits, is taken into account the complete field dependence of the resistance can be explained. Similar results are expected for the second proposed Fermi surface.[22]

In the DW phase the large magnetoresistance oscillates as the orientation of the magnetic field relative to the most conducting planes is varied [angle-dependent magnetoresistance oscillations (AMRO)].[2] To explain this effect a reconstructed Fermi surface consisting of two open sheets and many small ''lens'' orbits (Fig. 2) has been proposed.[20] The sheets give rise to a large magnetoresistance, except when the current

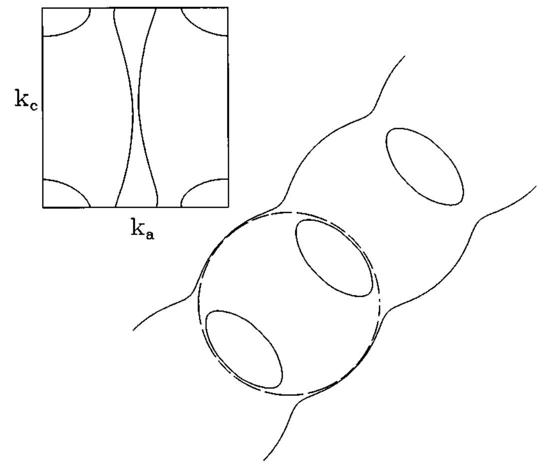

FIG. 2. One possible reconstruction of the Fermi surface by the periodic potential due to the density wave. The inset shows the calculated Fermi surface (Ref. 26) for the Tl salt at room temperature. It consists of quasi-two-dimensional cylinders for holes and quasi-one-dimensional open sheets for electrons. The main figure shows the reconstructed hole Fermi surface used in our calculations. It now comprises open orbits and closed orbits. The former produce a large magnetoresistance at low fields. At high fields magnetic breakdown results in only closed orbits (dashed lines). The open electron Fermi surface shown in the inset disappears due to the opening of an energy gap.

direction is perpendicular to the sheets. At low fields the magnetoresistance will increase quadratically with field. This model has been used to give a quantitative description of the AMRO for fields up to about 15 T.[23] However, these calculations do not include magnetic breakdown and cannot explain the decrease in resistance with increasing fields above 15 T.

There are several problems with the Fermi surface reconstruction shown in Fig. 2. The existence of open sheets depends on a delicate balance between the size and shape of the Fermi surface and the direction of the DW wave vector. There is experimental[21,24,25] and theoretical[26] evidence that the desired conditions are not met. Uji *et al.*[21] proposed an alternative reconstructed Fermi surface with no open sheets. Compensated electron and hole pockets produce a large magnetoresistance which will be reduced by magnetic breakdown.[5] Due to the above problems, Yoshioka[27] proposed an explanation for the AMRO that does not require reconstruction of the Fermi surface.[28]

The effect of magnetic breakdown on magnetoresistance has been considered in detail by Pippard[29] and Falicov and Sievert.[30] They quantitatively described the shape of the magnetoresistance curves for zinc and magnesium,[29,31] which are similar to those in Fig. 1. We have calculated the magnetoresistance for the model Fermi surface shown in Fig. 2 using the formalism of Falicov and Sievert.[30,32] The ratio of the resistance in a field H, $\rho(H)$, to the zero-field resistance ρ_0 depends on the dimensionless quantities H/H_0 and $eH_0\tau/m^*$, where τ is the scattering time (assumed to be the same at all points on the Fermi surface), e is the electronic charge, m^* is the effective mass, and H_0 is the magnetic breakdown field[29]

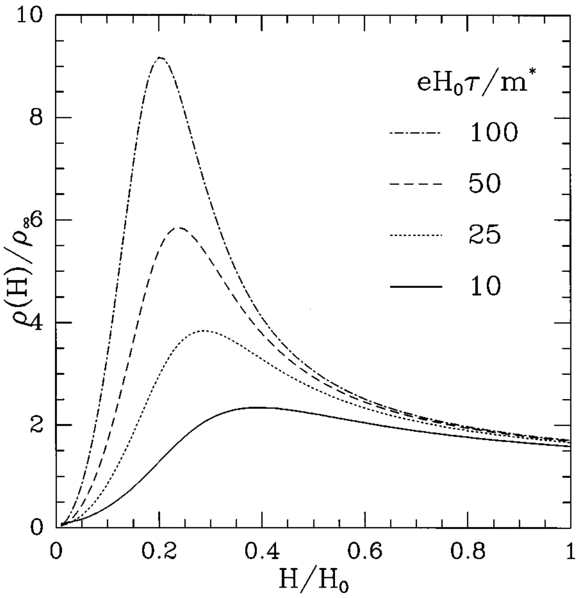

FIG. 3. Magnetic-field dependence of the resistance for the Falicov-Sievert model with the Fermi surface shown in Fig. 2. The calculation is for a field perpendicular to the plane and the current parallel to the open sheet of the reconstructed Fermi surface. The upper curves correspond to larger scattering times τ, i.e., lower temperatures or higher-quality samples. The magnetic field is normalized to the magnetic breakdown field H_0 defined in Eq. (1). The resistance is normalized to its value at high fields given by Eq. (2). A similar field dependence is expected for the alternative Fermi surface proposed by Uji *et al.* (Ref. 21).

$$H_0 = \frac{\pi E_g^2}{2e\hbar v_F^2 \sin 2\theta}, \quad (1)$$

where E_g is the energy gap and v_F is the Fermi velocity, and $\cos\theta = Q/2k_F$.[33] The probability of magnetic breakdown occurring (i.e., a hole tunneling between the two pieces of Fermi surface) is $\exp(-H_0/H)$. At high fields ($H \gg H_0$) complete breakdown occurs, the holes simply perform closed orbits and the resistance is independent of field and for the model Fermi surface[30] (with $\theta = \pi/4$)

$$\rho_\infty = \rho_0\left(1 + \frac{4eH_0\tau}{\pi m^*}\right). \quad (2)$$

The holes experience an effective scattering rate[30] $\tau^{-1} + 4eH_0/\pi m^*$ where the second term represents additional scattering due to magnetic breakdown.[34]

Figure 3 shows the field dependence of the resistance for values of $eH_0\tau/m^*$ ranging from 10 to 100. The current is parallel to the open Fermi surface and the field is perpendicular to the plane. No magneto-oscillations are present because the model is semiclassical. Note the following features, all similar to that observed in $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4[M=\mathrm{K,Rb,Tl}]$. (i) For low fields the resistance increases quadratically with field. (ii) There is a maximum at a field H_{max}. (iii) Above about $0.8H_0$ the resistance depends weakly on the field and on the scattering rate. (iv) As the scattering rate decreases the maximum value of the resistance increases and H_{max} decreases.

It should be noted that the current orientation in our calculation is *not* the same as in the experiment. In the experiment the current and field were set parallel to the least conducting direction, as others have done, because this produces a large signal-to-noise ratio. In such a configuration no Lorentz force acts on the electrons and so no classical magnetoresistance and no oscillations are expected. Yet, for reasons that are not understood,[5] the data is similar to that seen when the current is in the most conducting plane.[8–10,35]

Comparing our data for Tl to the theory gives values for τ and H_0 of $(3\pm2)\times10^{-12}$ sec and 60 ± 20 T, respectively. The value of τ corresponds to a Dingle temperature of 0.4 ± 0.3 K. This value is comparable to values of about 0.2 K deduced from the field dependence of SdH and dHvA oscillations *above* H_k for the K salt.[36] This value is much smaller than the values of about 3–4 K deduced from the field dependence of the oscillations *below* H_k.[36] This may be reasonable because the field dependence of the closed hole orbit (also known as the α orbit) below H_k will be dominated by magnetic breakdown and not scattering.[37]

The temperature dependence of the magnetoresistance might appear to be due to the temperature dependence of the scattering rate. If so the scattering rate in the Tl salt should change by a factor of about 2 as the temperature changes from 0.36 to 4.4 K. However, no such change is observed in the zero-field resistance.[38]

The deduced value of H_0 and (i) gives a value for E_g of about 10 ± 2 meV.[39] It is important to note that the *same* periodic potential (due to the DW wave) reconstructs the hole Fermi surface and produces an energy gap E_1 on the quasi-one-dimensional electron Fermi surface. Elementary band theory[40] implies $E_1 = E_g$. As far as we are aware E_1 has not been determined previously. A rough estimate of this gap can be made by noting that for a quasi-one-dimensional system (with no coexisting two-dimensional Fermi surface) mean-field theory implies $E_1 = 3.52k_BT_{\mathrm{DW}}$. A transition temperature of $T_{\mathrm{DW}} = 9$ K gives $E_1 = 3$ meV. However, in typical quasi-one-dimensional materials the gap is actually two to five times that predicted by this relation (see Table II in Ref. 41), probably due to fluctuations reducing the transition temperature. Hence the value we deduce for the breakdown field is quite reasonable. For the Rb salt we deduce a slightly larger value of H_0, and thus E_1, consistent with the trend in transition temperatures (9 K versus 12 K).

That we can describe the field dependence of the resistance using the magnetic breakdown model applied to the reconstructed Fermi surface has important implications for the phase diagram and what one deduces from magnetoresistance measurements. Within our framework the transition at the kink field represents only a small change in the magnetoresistance. In contrast, for the Tl salt it has been suggested that because the resistance decreases between H_{max} and H_k this field region represents a different phase.[9,35] Also, it has been suggested that the absence of AMRO above H_k denotes destruction of the reconstructed Fermi surface.[18] However, within our model this may not be the case: the Fermi surface may still be reconstructed but due to magnetic breakdown the open Fermi surface has little effect on the resistance. The question of the nature of the high-field phase will be considered in more detail elsewhere.[6]

In conclusion, we have presented measurements of the field and temperature dependence of the resistance of $(\mathrm{BEDT\text{-}TTF})_2M\mathrm{Hg(SCN)}_4[M=\mathrm{Rb,Tl}]$ up to 51 T and shown how the field dependence can be explained in terms of magnetic breakdown and a reconstructed Fermi surface in the density-wave phase. Our successful explanation has important implications for the phase diagram. It is not necessary to assume that there is a new phase between H_{max} and H_k, and the high-field phase may not be the same as the zero-field metallic phase.

Work at UNSW was supported by the Australian Research Council. GJA and JSB were supported in part by NSF Grant No. DMR 92-14889. We thank P. M. Sievert, J. Singleton, S. Uji, and T. Ziman for helpful discussions. We thank M. V. Kartovsnik for sending us a well-characterized sample of $(\mathrm{BEDT\text{-}TTF})_2\mathrm{TlHg(SCN)}_4$. Figure 2 was produced by D. Scarratt. T. Ziman and E. Canadell provided data for the inset.

*Electronic address: ross@newt.phys.unsw.edu.au

[1] For a review, see T. Ishiguro and K. Yamaji, *Organic Superconductors* (Springer-Verlag, Berlin, 1990).

[2] J. S. Brooks, Mater. Res. Soc. Bull. **18**, 29 (1993).

[3] F. L. Pratt *et al.*, Phys. Rev. Lett. **74**, 3892 (1995).

[4] J. S. Brooks *et al.*, in *Physical Phenomena at High Magnetic Fields II*, edited by Z. Fisk *et al.* (World Scientific, Singapore, 1996).

[5] G. J. Athas, Ph.D. thesis, Boston University, 1996.

[6] R. H. McKenzie (unpublished).

[7] J. S. Brooks *et al.*, Phys. Rev. Lett. **69**, 156 (1992).

[8] T. Osada *et al.*, Phys. Rev. B **41**, 5428 (1990).

[9] T. Sasaki and N. Toyota, Solid State Commun. **82**, 447 (1992).

[10] S. Uji *et al.*, Solid State Commun. **88**, 683 (1993).

[11] G. J. Athas *et al.*, Synth. Met. **70**, 843 (1995).

[12] S. Uji *et al.*, Phys. Rev. B (to be published).

[13] R. G. Clark *et al.*, Physica B **201**, 565 (1994).

[14] R. H. McKenzie *et al.*, Surf. Sci. (to be published).

[15] J. S. Brooks *et al.*, Physica B **216**, 380 (1996).

[16] J. S. Brooks *et al.*, Phys. Rev. B **52**, 14 457 (1995).

[17] M. V. Kartovsnik *et al.*, J. Phys. (France) I **4**, 159 (1994).

[18] J. Caulfield *et al.*, Phys. Rev. B **51**, 8325 (1995).

[19] H. Mori *et al.*, Bull. Chem. Soc. Jpn. **63**, 2183 (1990); L. Ducasseand A. Frisch, Solid State Commun. **91**, 201 (1994).

[20] M. V. Kartovsnik *et al.*, J. Phys. (France) I **3**, 1187 (1993); J. Phys., Condens. Matter **6**, L479 (1994).

[21] S. Uji *et al.*, J. Phys., Condens. Matter **6**, L539 (1994).

[22] It has previously been suggested (Refs. 8 and 10) that the field dependence can be explained in terms of magnetic breakdown. However, this earlier work assumed that the breakdown was between the open and closed Fermi surfaces in the inset of Fig. 2 (producing what is known as the β orbit) and involves a breakdown field two orders of magnitude larger than observed.

[23] Y. Iye *et al.*, J. Phys. Soc. Jpn. **63**, 674 (1994); S. J. Blundell and J. Singleton, Phys. Rev. B **53**, 5609 (1996).

[24] A. E. Kovalev *et al.*, Solid State Commun. **89**, 575 (1994).

[25] C. Haworth *et al.* (unpublished).

[26] M. Gusmão and T. Ziman (unpublished).

[27] D. Yoshioka, J. Phys. Soc. Jpn. **64**, 3168 (1995).

[28] A many-body explanation of the AMRO in $(\mathrm{TMTSF})_2\mathrm{PF}_6$ has been given by S. P. Strong, D. G. Clarke, and P. W. Anderson [Phys. Rev. Lett. **73**, 1007 (1994)].

[29] A. B. Pippard, *Magnetoresistance in Metals* (Cambridge, Cambridge, 1989).

[30] L. Falicov and P. R. Sievert, Phys. Rev. **138**, A88 (1965).

[31] D. Shoenberg, *Magnetic Oscillations in Metals*, (Cambridge, Cambridge, 1984).

[32] P. R. Sievert, Phys. Rev. **161**, 637 (1967).

[33] For simplicity we assume $\theta=\pi/4$. Figure 2 in Ref. 30 shows that varying θ produces only small changes in the shape of the magnetoresistance curve.

[34] For the model Fermi surface considered here magnetic breakdown has no effect on the Hall resistivity. For all fields it is given by H/ne where n is the density of holes. Note that if the sample purity is sufficiently great that $eH_0\tau \gg m^*$ then $\rho_\infty \sim H_0/ne$ and the ratio of the resistance to the Hall resistance will be roughly H_0/H. Hall measurements (Ref. 38) are consistent with this if $H_0 \sim 20$ T.

[35] T. Sasaki and N. Toyota, Phys. Rev. B **49**, 10 120 (1994).

[36] N. Harrison *et al.*, Phys. Rev. B **52**, 5584 (1995).

[37] If so then the amplitude of the oscillations $\sim\exp(-2H_0/H)$ (Ref. 31, p. 343 ff.). This means the Dingle temperature of 3–4 K (Ref. 36) corresponds to $H_0 \simeq$ 60–80 T. Although the consistency of this with our independent estimate of H_0 is appealing, this argument would also predict the same field dependence for the first and second harmonic, contrary to experiment.[36]

[38] T. Sasaki, S. Endo, and N. Toyota, Phys. Rev. B **48**, 1928 (1993).

[39] The Fermi velocity was estimated from the Fermi wave vector k_F calculated from the area of the hole Fermi surface implied by the frequency[14] (670 T) of Shubnikov de Haas oscillations (Ref. 31). We used an effective mass $m^*=2.7m_e$, given by the temperature dependence of the SdH oscillations (Ref. 36).

[40] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976), p. 158.

[41] R. H. McKenzie, Phys. Rev. B **52**, 16 428 (1995).