Eur. Phys. J. B **1**, 295–300 (1998)

THE EUROPEAN PHYSICAL JOURNAL B

Characterization of the Fermi surface of the organic superconductor β''-$(ET)_2SF_5CH_2CF_2SO_3$ by measurements of Shubnikov-de Haas and angle-dependent magnetoresistance oscillations and by electronic band-structure calculations

D. Beckmann[1], S. Wanka[1], J. Wosnitza[1,a], J.A. Schlueter[2], J.M. Williams[2], P.G. Nixon[3], R.W. Winter[3], G.L. Gard[3], J. Ren[4], and M.-H. Whangbo[4]

[1] Physikalisches Institut, Universität Karlsruhe, Engesserstrasse 7, 76128 Karlsruhe, Germany
[2] Chemistry and Materials Science Divisions, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439, USA
[3] Department of Chemistry, Portland State University, Portland, Oregon 97207-0751, USA
[4] Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, USA

Received: 3 March 1997 / Revised: 5 May 1997 / Received in final form: 5 November 1997 / Accepted: 10 November 1997

Abstract. The electronic structure of the quasi two-dimensional (2D) organic superconductor β''-$(ET)_2SF_5CH_2CF_2SO_3$ was examined by measuring Shubnikov-de Haas (SdH) and angle-dependent magnetoresistance (AMRO) oscillations and by comparing with electronic band-structure calculations. The SdH oscillation frequencies follow the $1/\cos\Theta$ angular dependence expected for a 2D Fermi surface (FS), and the observed fundamental frequency shows that the 2D FS is 5% of the first Brillouin zone in size. The AMRO data indicate that the shape of the 2D FS is significantly non-circular. The calculated electronic structure has a 2D FS in general agreement with experiment. From the temperature and angular dependence of the SdH amplitude, the cyclotron and band effective masses were estimated to be $m_c = (1.9 \pm 0.05)\, m_e$ and $m_b = (3.90 \pm 0.05)\, m_e/g$, where g is the conduction electron g factor and m_e the free electron mass. The band effective mass is estimated to be $m'_b = 1.07\, m_e$ from the calculated electronic band structure.

PACS. 71.18.+y Fermi surface: calculations and measurements; effective mass, g factor – 74.70.Kn Organic superconductors

1 Introduction

With various monovalent anions X^-, the donor molecule bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF abbreviated ET) forms a number of superconducting salts $(ET)_2X$ [1], with κ-$(ET)_2Cu[N(CN)_2]Cl$ showing the highest superconducting critical temperature ($T_c = 12.8$ K under ∼300 bar) [2]. In these 2:1 salts, layers of $ET^{0.5+}$ cations alternate with layers of the anion X^-, and ET molecules exhibit a number of distinct packing motifs [1]. Their metallic properties, which originate from the partially filled bands of the cation layers, can be quasi two-dimensional (2D).

Recently, in a new direction for synthesis in organic superconductors, several superconducting salts of ET were prepared with large discrete anions [3–5]. In the salts of anion $M(CF_3)_4^-$ (M = Cu, Ag, Au), solvent molecules (*e.g.*, 1,1,2-trihaloethane) are incorporated in the crystal structures, and the loss of these molecules from a sample lowers the superconducting volume fraction but not T_c [3]. The new superconductor β''-$(ET)_2SF_5CH_2CF_2SO_3$ [4,5] contains a large anion but no solvent molecules. According to ac-susceptibility measurements, the superconducting onset temperature of this salt is ∼5.2 K [4,5]. Another β''-phase superconductor is β''-$(ET)_4H_2OFe(C_2O_4)_3{\cdot}C_6H_5CN$ with $T_c \approx 7$ K [6], which exhibits both superconductivity and paramagnetism, the latter arising from the Fe atoms in the anion layer. So far little experimental information is available about the electronic structures of these superconducting β'' phases. Based on magnetic quantum oscillations, direct determination of band-structure parameters was possible for β''-$(ET)_2AuBr_2$ [7,8], but this salt is not a superconductor and is believed to undergo an antiferromagnetic phase transition at $T \approx 20$ K. Several electronic band-structure calculations have been carried out for β''-phase salts of ET [5,8–10].

---

[a] e-mail: `Jochen.Wosnitza@physik.uni-karlsruhe.de`

To determine experimentally the Fermi surface (FS) and band-structure parameters of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$, we attempted to detect de Haas–van Alphen (dHvA) signals with the modulation-field technique and with a torque magnetometer in fields up to 15 T. This attempt was unsuccessful, due likely to the low sensitivity of these techniques to small dHvA frequencies. However, we successfully observed Shubnikov-de Haas (SdH) signals and angle-dependent magnetoresistance oscillations (AMRO). In the present work, we present results of the SdH and AMRO measurements and discuss these results based on the electronic band structure of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ calculated by use of the extended Hückel tight binding method [11].

2 Experimental

A single-crystal sample of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ was grown at Argonne by an electrocrystallization process which is described in detail elsewhere [5]. Our measurements were carried out for a sample of size $\sim 500\times500\times100\,\mu$m, a piece chipped from a large (2.4 mg) high-quality single crystal. The resistance of the sample was measured in a ^{3}He top-loading cryostat with a standard low-frequency four-point ac method. Gold wires were attached to the sample with gold paint, with the current directed perpendicular to the highly conducting plane of the sample. Care was taken to avoid heating of the sample by the applied current. SdH measurements were carried out in magnetic fields of up to 13 T. The sample was rotated *in situ*, and the angle Θ between the magnetic field and the c^*-direction of the sample was varied with an accuracy of better than 0.1°.

Theories explaining SdH oscillations are typically formulated in terms of conductance. Thus, the resistance data were analyzed as follows: the conductance σ was calculated by inverting the resistance, the steady part of the conductance (σ_{steady}) was fitted by a polynomial, the relative conductance oscillations ($\Delta\sigma = \sigma/\sigma_{\text{steady}} - 1$) were calculated by using the polynomial, and the Fourier transform was applied to these conductance oscillation data. To be rigorous, calculations of a conductance require the inversion of a complete resistance tensor. By simply inverting the resistance data, our analysis neglected the oscillatory part of the Hall resistivity. The latter is believed to be small in ordinary metals but may play an important role in 2D systems. However, when $\Theta = 0$, the current involved in our experiment is parallel to the magnetic field, so the Hall effect should be zero.

3 Results

The sample showed a monotonic decrease in resistance from room temperature down to the superconducting onset temperature, with a residual resistance ratio $R(300\,\text{K})/R(6\,\text{K}) \approx 220$. Magnetization measurements of the sample showed a superconducting transition at $T_c = 4.5\,\text{K}$. SdH oscillations were observed at fields above 7 T for angles $|\Theta| < 62°$. Figure 1 shows the resistance of the sample at $T = 0.44\,\text{K}$ when the applied magnetic field B is perpendicular to the ab plane (*i.e.*, $\Theta = 0$). A single frequency is observed without any beating pattern. The Fourier transform of the relative conductance oscillations (inset of Fig. 1) reveals the spectral purity of the signal, *i.e.*, one fundamental SdH frequency ($F = 200\,\text{T}$) and its second harmonic. There is no indication of an anomalously high harmonic content, although the latter is commonly observed in other 2D organic superconductors.

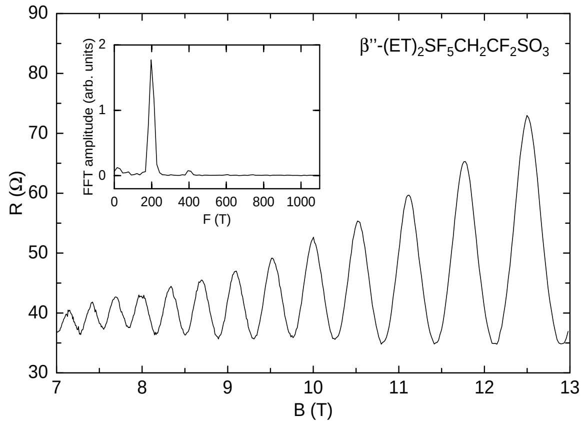


Fig. 1. Resistance of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ as a function of applied magnetic field at $\Theta = 0$. The inset shows the Fourier transform of the relative conductance oscillations (see text).

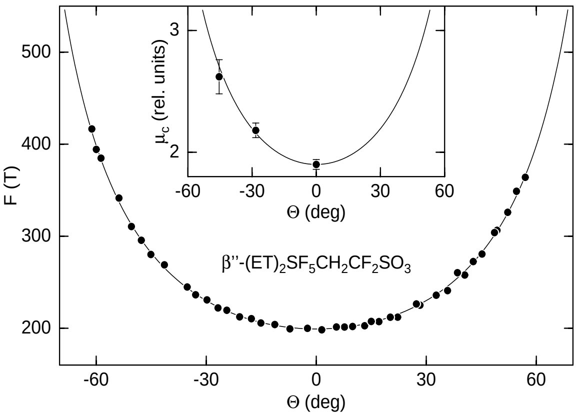


Fig. 2. Angular dependences of the SdH frequency F and the effective cyclotron mass $\mu_{\text{c}} = m_{\text{c}}/m_{\text{e}}$ (inset). The solid lines are fits to the expressions $F = F_0/\cos\Theta$ and $\mu_{\text{c}} = \mu_{\text{c}0}/\cos\Theta$, respectively.

When the magnetic field is inclined (*i.e.*, $\Theta \neq 0$) the SdH frequency shifts upward while the oscillation amplitude becomes smaller initially. Neither a beating pattern nor a second fundamental frequency was observed at any angle Θ. The angular dependence of the SdH frequency is shown in Figure 2. The solid line is a fit using the expression $F = F_0/\cos\Theta$, which leads to the value $F_0 = (199\pm2)\,\text{T}$. This F_0 value corresponds to an extremal

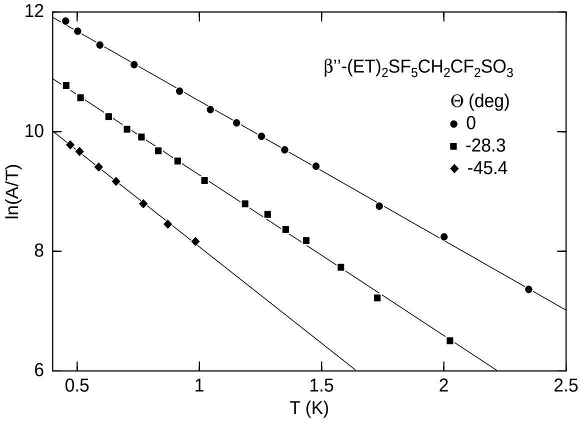


Fig. 3. Temperature dependence of the A/T term determined at three different rotation angles Θ, where A refers to the SdH amplitude. The solid lines are fits according to (1) as explained in the text.

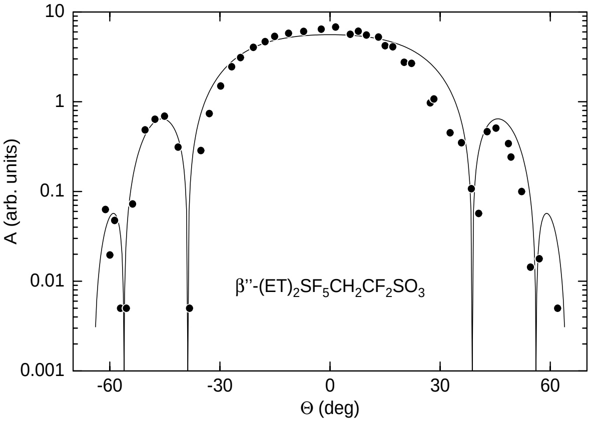


Fig. 4. Angular dependence of the fundamental SdH amplitude A at $T = 0.45\,\mathrm{K}$ in a half-logarithmic scale. The solid line is a fit according to (3) showing two spin-splitting zeros.

FS cross section of 0.019 Å^{-2}, *i.e.*, 5% of the first Brillouin zone (based on the crystal structure data at 123 K [5]). For a quasi-2D FS with a slight warping along its axis, a beating pattern is expected with a maximum frequency difference $\Delta F_{\max} = 4F_0(t/\epsilon_F)$, where t is the inter-layer transfer integral and ϵ_F is the Fermi energy [12–14]. The absence of beating in a field range between 7 T and 13 T implies that $t/\epsilon_F < 1/150$.

The temperature dependence of the SdH amplitude A was examined at three different angles, as summarized in Figure 3. The oscillations were observed at temperatures up to 2.5 K for $\Theta = 0$. The solid lines are fits to the Lifshitz-Kosevich (LK) expression [15]

$$A/T \propto \exp(-\alpha\mu_c T/B), \tag{1}$$

where $\alpha = 2\pi^2 k_B m_e/e\hbar = 14.69\,\mathrm{T/K}$, and μ_c is the effective cyclotron mass m_c/m_e. In (1) the hyperbolic sine term of the original LK formula is approximated by a single exponential term [16]. The data are in excellent agreement with the predictions of LK theory over the whole temperature range and led to the μ_c values of 1.9 ± 0.05, 2.18 ± 0.06, and 2.62 ± 0.14 at $\Theta = 0$, -28.3, and $-45.4°$, respectively. The angular dependence of μ_c is consistent with the $1/\cos\Theta$ behavior expected for 2D systems (inset of Fig. 2).

Lifshitz–Kosevich theory for SdH oscillations [17] predicts that the oscillation amplitude A depends on the field strength B as

$$A \propto \sqrt{B}\exp(-\alpha\mu_c(T + T_D)/B), \tag{2}$$

where T_D is the Dingle temperature. The analysis of our data with use of this expression leads to $T_D = 0.6\,\mathrm{K}$. The rate of electronic scattering calculated from this temperature is $1/\tau = 2\pi k_B T_D/\hbar = 4.9 \times 10^{11}\,\mathrm{s}^{-1}$.

The angular dependence of the SdH amplitude for sweeps between 7 T and 13 T at a fixed temperature (0.45 K) is shown in Figure 4. Two spin-splitting zeros occur at $|\Theta| = 38.8$ and $56.1°$. This enables the determination of the product $g\mu_b$, where g is the conduction electron g-factor, and μ_b the effective mass m_b/m_e. This product is renormalized by electron-electron interaction but not renormalized by electron-phonon interaction [15,18]. Since both μ_c and μ_b are proportional to $1/\cos\Theta$, LK theory gives the following relationship

$$A \propto \frac{1}{\cos\Theta}\exp\left(\frac{-\alpha\mu_c(T + T_D)}{B}\right)\left|\cos\left(\frac{\pi g\mu_b}{2}\right)\right|. \tag{3}$$

This expression was employed to fit the data points of Figure 4 treating $g\mu_b$ and T_D as free parameters thereby leading to the results, $g\mu_b = 3.90 \pm 0.05$ (at $\Theta = 0$) and $T_D \approx 1.5\,\mathrm{K}$. This T_D is somewhat higher than the value estimated from (2) (*i.e.*, $T_D \approx 0.6\,\mathrm{K}$), which reflects the uncertainty in the exact determination of this quantity.

The angle-dependent magnetoresistance oscillation (AMRO) data determined at ~0.4 K under magnetic field 7 T are presented in Figure 5. So far only one field-rotation plane, *i.e.*, the plane perpendicular to $b^\star$ (±3°), could be investigated. A slightly asymmetric pattern with four maxima (indicated by arrows) is observed. A quasi-2D metal can exhibit AMRO when the Fermi cylinder is slightly warped along its axis [13,14]. From the distance of the two maxima, the Fermi wave vector parallel to the plane of rotation is estimated [13] to be $k_{F\parallel} = 0.24\,$Å^{-1}. This is significantly larger than the value $k_F = 0.078\,$Å^{-1} one may derive assuming that the 2D FS responsible for F_0 is circular. When the 2D FS pocket is approximated by an ellipse, the Fermi wave vector perpendicular to the plane of rotation would be $k_{F\perp} = 0.1 k_{F\parallel}$ from the observed pocket size. If the rotation plane was such that $k_{F\parallel}$ is not parallel to the long axis of the ellipse, the estimated $k_{F\perp}$ values become even smaller. However, for a definite determination of the in-plane FS shape a systematic AMRO study is necessary.

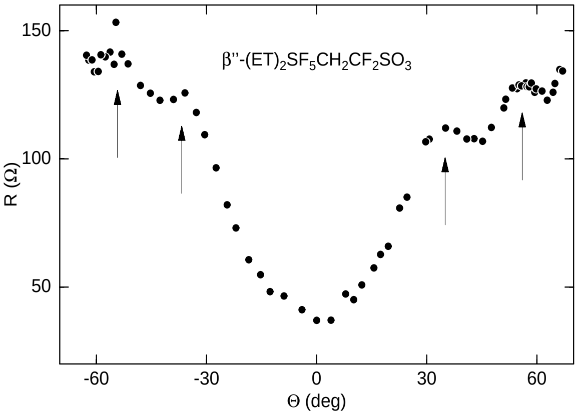


Fig. 5. Angular dependence of the resistance at $T \approx 0.4\,\mathrm{K}$ under $B = 7\,\mathrm{T}$. The field was rotated approximately perpendicular to $b^\star$.

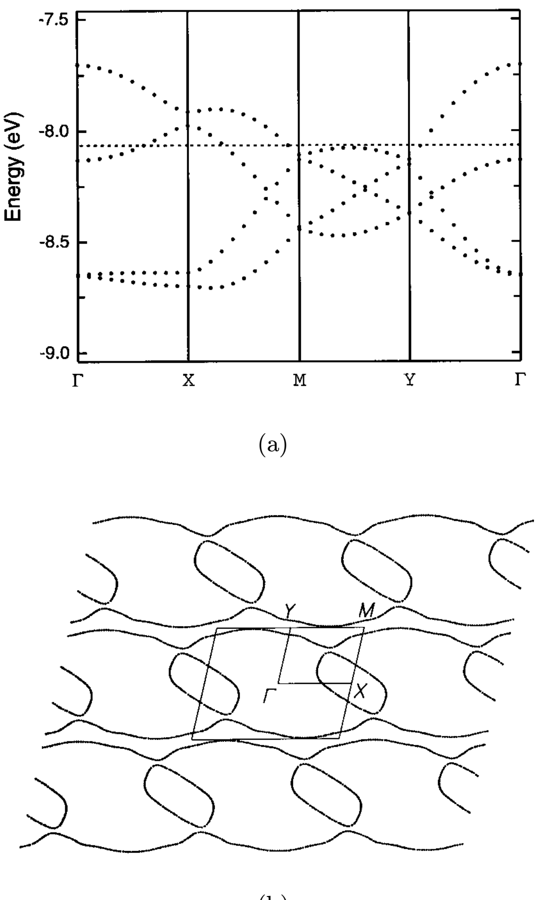
4 Electronic band structure and discussion

The recent electronic band-structure study of β''-$(\mathrm{ET})_2$-$\mathrm{SF_5CH_2CF_2SO_3}$ showed that it has two FS's, a pair of warped 1D sheets and a distorted 2D cylinder, and that the cross-section area of the 2D FS cylinder is about 25% of the first Brillouin zone (FBZ) [5]. The present results are consistent with this picture, but the observed cross-section area (5%) is much smaller than predicted. The extended Hückel tight binding calculations of Geiser *et al.* [5], though reported the use of double-zeta Slater type orbitals (STO's) [19], actually employed single-zeta STO's. Therefore, to access a more realistic discrepancy between theory and experiment, it was crucial to re-examine the electronic structure of β''-$(\mathrm{ET})_2\mathrm{SF_5CH_2CF_2SO_3}$ with use of double-zeta STO's.

Figure 6a shows the dispersion relations of the four highest-lying bands calculated for β''-$(\mathrm{ET})_2\mathrm{SF_5CH_2CF_2SO_3}$ with use of double-zeta STO's. The highest two bands are partially filled and give rise to the FS's shown in Figure 6b. As in the case of single-zeta STO calculations [5], the FS's consist of a 2D hole pocket centered at X and a pair of wavy lines straddling along the Y−M line. With double-zeta STO calculations, the size of the 2D hole pocket is considerably smaller (*i.e.*, 14.8% of the FBZ) and hence is much closer to the experimental value. If the shape of the 2D pocket is approximated by a rectangle, the ratio of the long-side to short-side length is calculated to be ∼ 2.2. The STO calculations underestimate the ellipticity and overestimate the FS size by a factor of 3. However, the direction of the calculated long axis of the 2D pocket lies only slightly (∼ 20°) out of the experimental field-rotation plane. It remains to be understood why such a large discrepancy between the calculated and measured FS is observed.

The band effective mass m'_b associated with the 2D FS pocket can be calculated by use of the expression

$$m'_\mathrm{b} = \frac{\hbar^2}{2\pi}\frac{\mathrm{d}S}{\mathrm{d}\epsilon}, \tag{4}$$



(a)

(b)

Fig. 6. (a) Dispersion relations of the four highest occupied bands calculated for β''-$(\mathrm{ET})_2\mathrm{SF_5CH_2CF_2SO_3}$, where the dashed line refers to the Fermi level, $\Gamma = (0, 0)$, $\mathrm{X} = (a^\star/2, 0)$, $\mathrm{Y} = (0, b^\star/2)$, and $\mathrm{M} = (a^\star/2, b^\star/2)$. (b) FS's calculated for β''-$(\mathrm{ET})_2\mathrm{SF_5CH_2CF_2SO_3}$. The closed pockets located at X and its equivalent points are hole surfaces, and the wavy lines straddling along the Y − M direction are electron surfaces.

where S is the area of the 2D pocket in the FBZ. From the calculated electronic structure and (4), m'_b is estimated to be $1.07\,m_\mathrm{e}$. This value is considerably smaller than $\sim 1.9\,m_\mathrm{e}$ obtained from the temperature dependence of the SdH amplitude (*cf.* Fig. 2).

The effective cyclotron mass $m_\mathrm{c} \approx 2m_\mathrm{e}$ (for $\Theta = 0$) which lies within the range usually found in organic metals [12] is obviously enhanced by many-body interactions. In organic metals both electron-electron and electron-phonon interactions are important. Based on the BCS mechanism of superconductivity electron-phonon coupling constants λ of the ET-based superconductors are estimated to be of the order 0.5 to 1.5 [1,20]. Enhanced g factors are frequently observed in magnetic quantum oscillation studies of organic superconductors and indicate the importance of electron correlations in these materials [21]. The m_c enhancement due to electron-phonon (λ) and electron-electron (λ_ee) interaction may be written as

$m_c = (1+\lambda)(1+\lambda_{ee})m'_b = (1+\lambda)m_b$ [15,22]. The g value in (3) is then given by $g = g_{ESR}/(1+\lambda'_{ee})$, where $g_{ESR} \approx 2$ is the g value from ESR measurements and λ'_{ee} is the renormalization due to electron-electron interaction which is different from λ_{ee} and usually is small and negative [15]. From the magnetic quantum oscillations alone the values of λ and λ_{ee} cannot unambiguously be extracted. However, the value $\lambda = 1.1 \pm 0.1$, estimated from recent specific-heat measurements [23] would indicate only a minor renormalization of m_c due to electron-electron interaction, but a strong renormalization of $g \approx 3.9$. In an alternative extreme, one may assume that electron-electron interactions do not cause any g factor enhancement. Then $\lambda_{ee} \approx 0.9$ and $\lambda \approx 0$ would be estimated which, however, is in contrast to the specific-heat result. It is most likely that g and m_c are both renormalized by electron-electron interactions.

The observation of AMRO's indicates that the Fermi cylinder is slightly warped along its axis [14]. Such a warping means that there are two extremal cross sections of the FS, which can give rise to a beating pattern in the SdH or dHvA oscillations as observed, *e.g.*, in β_H-(ET)$_2$I$_3$ and β-(ET)$_2$IBr$_2$ [12,21,24,25]. Since no beating was observed, the warping and hence the transfer integral between the highly conducting planes must be very small. This is related, most likely, to the large interlayer separation resulting from the large anion and the resulting packing motif [5].

5 Concluding remarks

We have presented the first magnetic quantum oscillation study of the newly synthesized organic superconductor β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$. The SdH oscillation frequencies follow the $1/\cos\Theta$ angular dependence expected for a 2D FS, and the fundamental frequency corresponds to 5% of the FBZ. The observed AMRO's indicate that the 2D FS has the shape of a rounded rectangle. These experimental findings are in general agreement with the calculated 2D FS although considerable quantitative discrepancies are found. The effective masses derived from magnetoresistance measurements are $m_c = (1.9 \pm 0.05)m_e$ and $m_b = (3.9 \pm 0.05)m_e/g$. Both the g and m_b terms may be renormalized by electron-electron interactions. It remains a challenge to disentangle the two contributions.

β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ exhibits transport properties and electronic structures similar to those found for the α-(ET)$_2M$Hg(SCN)$_4$ (M = K, Rb, Tl, NH$_4$) phases [26–28]. β''-phase salts of ET are interesting candidates for further systematic investigations for the interplay between FS parameters, many-body interactions and the different ground states in organic metals. It is of interest to fully characterize the AMRO's of β''-(ET)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ and examine whether this salt undergoes a magnetic breakdown or a FS reconstruction under high magnetic field.

We thank H. Henke for the help in crystal orientation. Work at Karlsruhe was supported by the Deutsche Forschungsgemeinschaft under contract Wo444/2-2. Work at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Divisions of Chemistry and Materials Sciences, under contract No. W-31-109-ENG-38. Work at Portland State University is supported by NSF (Che-9632815) and the Petroleum Research Fund (ACS-PRF # 31099-AC1). Work at North Carolina State University was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U S. Department of Energy, under grant DE-FG05-86ER45259.

References

1. J.M. Williams, J.R. Ferraro, R.J. Thorn, K.D. Carlson, U. Geiser, H.H. Wang, A.M. Kini, M.-H. Whangbo, *Organic Superconductors: Synthesis, Structure, Properties, and Theory* (Englewood Cliffs: Prentice Hall, 1992).
2. J.M. Williams, A.M. Kini, H.H. Wang, K.D. Carlson, U. Geiser, L.K. Montgomery, G.J. Pyrka, D.M. Watkins, J.M. Kommers, S.J. Boryschuk, A.V. Strieby Crouch, W.K. Kwok, J.E. Schirber, D.L. Overmyer, D. Jung, M.-H. Whangbo, Inorg. Chem. **29**, 3272 (1990).
3. J.A. Schlueter, K.D. Carlson, U. Geiser, H.H. Wang, J.M. Williams, W.K. Kwok, J.A. Fendrich, U. Welp, P.M. Keane, J.D. Dudek, A.S. Komosa, Physica C **233**, 379 (1994).
4. J.A. Schlueter, U. Geiser, J.M. Williams, J.D. Dudek, M.E. Kelly, J.P. Flynn, R.R. Wilson, H.I. Zakowicz, P.P. Sche, D. Naumann, T. Roy, P.G. Nixon, R.W. Winter, G.L. Gard, Synth. Metals **85**, 1453 (1997).
5. U. Geiser, J.A. Schlueter, H.H. Wang, A.M. Kini, J.M. Williams, P.P Sche, H.I. Zakowicz, M.L. VanZile, J.D. Dudek, P.G. Nixon, R.W. Winter, G.L. Gard, J. Ren, M.-H. Whangbo, J. Am. Chem. Soc. **118**, 9996 (1996).
6. M. Kurmoo, A.W. Graham, P. Day, S.J. Coles, M.B. Hursthouse, J. Caulfield, J. Singleton, F.L. Pratt, W. Hayes, L. Ducasse, P. Guionneau, J. Am. Chem. Soc. **117**, 12209 (1995).
7. S. Uji, H. Aoki, M. Tokumoto, A. Ugawa, K. Yakushi, Physica B **194-196**, 1307 (1994).
8. M. Doporto, J. Singleton, F.L. Pratt, J. Caulfield, W. Hayes, J.A.A.J. Perenboom, I. Deckers, G. Pitsi, M. Kurmoo, P. Day, Phys. Rev. B **49**, 3934 (1994); A.A. House, N. Harrison, S.J. Blundell, I. Deckers, J. Singleton, F. Herlach, W. Hayes, J.A.A.J. Perenboom, M. Kurmoo, P. Day, Phys. Rev. B **53**, 9127 (1996).
9. K. Kajita, Y. Nishio, S. Moriyama, W. Sasaki, R. Koto, H. Kobayashi, A. Kobayashi, Solid State Comm. **60**, 811 (1986).
10. T. Mori, F. Sakai, G. Saito, H. Inokuchi, Chem. Lett. **1986**, 1037 (1986).
11. M.-H. Whangbo, R. Hoffmann, J. Am. Chem. Soc. **100**, 6093 (1978).
12. J. Wosnitza, *Fermi Surfaces of Low-Dimensional Organic Metals and Superconductors* (Berlin, Heidelberg: Springer, 1996).
13. K. Yamaji, J. Phys. Soc. Jpn **58**, 1520 (1989); K. Yamaji, *The Physics and Chemistry of Organic Superconductors* (Berlin, Heidelberg: Springer 1990), p. 216.

14. M.V. Kartsovnik, V.N. Laukhin, S.I. Pesotskii, I.F. Schegolev, V.M. Yakovenko, J. Phys. I France **2**, 89 (1992).
15. D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge: Cambridge University Press, 1984).
16. Use of the hyperbolic sine form leads to the μ_c values that agree within error bars with those obtained by a single exponential term.
17. E.M. Lifshits, A.M. Kosevich, J. Phys. Chem. Sol. **4**, 1 (1958).
18. S. Engelsberg, G. Simpson, Phys. Rev. B **2**, 1657 (1970).
19. M.-H. Whangbo, J.M. Williams, P.C.W. Leung, M.A. Beno, T.J. Emge, H.H. Wang, K.D. Carlson, G.W. Crabtree, J. Am. Chem. Soc. **107**, 5815 (1985).
20. M.-H. Whangbo, J.M. Williams, A.J. Schultz, T.J. Emge, M.A. Beno, J. Am. Chem. Soc. **109**, 90 (1987).
21. J. Wosnitza, G. Goll, D. Beckmann, S. Wanka, D. Schweitzer, W. Strunz, J. Phys. I France **6**, 1597 (1996).
22. S.A. Ivanov, C.H. Mielke, T. Coefey, D.A. Howe, C.C. Agosta, B.W. Fravel, L.K. Montgomery, Phys. Rev. B **55**, 4191 (1997).
23. S. Wanka, J. Hagel, D. Beckmann, J. Wosnitza, J.A. Schlueter, J.M. Williams, P.G. Nixon, R.W. Winter, G.L. Gard, Phys. Rev. B, in press.
24. W. Kang, G. Montambaux, J.R. Cooper, D. Jérome, P. Batail, C. Lenoir, Phys. Rev. Lett. **62**, 2559 (1989).
25. D. Beckmann, S. Wanka, J. Wosnitza, D. Schweitzer, W. Strunz, Z. Phys. B **104**, 207 (1997).
26. S. Uji, T. Terashima, H. Aoki, J.S. Brooks, M. Tokumoto, N. Kinoshita, T. Kinoshita, Y. Tanaka, H. Anzai, Phys. Rev. B **54**, 9332 (1996).
27. R.H. McKenzie, G.J. Athas, J.S. Brooks, R.G. Clark, A.S. Dzurak, R. Newbury, R.P. Starrett, A. Skougarevsky, M. Tokumoto, N. Kinoshita, T. Kinoshita, Y. Tanaka, Phys. Rev. B **54**, R8289 (1996).
28. T. Sasaki, A.G. Lebed, T. Fukase, N. Toyota, Phys. Rev. B **54**, 12969 (1996).