Vol. 87 (1995) *ACTA PHYSICA POLONICA A* No. 4–5

Proceedings of the IV International Seminar on Organic Materials for Molecular Electronics,
Zajączkowo 1994

INVESTIGATIONS OF FERMI SURFACES AND EFFECTIVE MASSES OF THE ORGANIC SUPERCONDUCTORS (BEDO-TTF)$_2$ReO$_4$(H$_2$O) AND κ-(BEDT-TTF)$_2$I$_3$ BY SHUBNIKOV-DE HAAS AND DE HAAS–VAN ALPHEN MEASUREMENTS

D. Schweitzer, E. Balthes, S. Kahlich
3. Physik. Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

I. Heinen, H.J. Keller, W. Strunz
Anorg.-Chemisches Institut, Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

W. Biberacher
Walther Meissner Institut, Walther-Meissner-Str. 8, 85748 Garching, Germany

A.G.M. Jansen and E. Steep
High Magnetic Field Laboratory, MPI für Festkörperforschung
38042 Grenoble Cedex 9, France

The Fermi surfaces and effective masses of (BEDO-TTF)$_2$ReO$_4$(H$_2$O) and κ-(BEDT-TTF)$_2$I$_3$ were investigated by Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) measurements in magnetic fields up to 27 T in the temperature range from 0.5 K to 4.2 K. Two small closed pockets (0.7% and 1.5% of the first Brillouin zone) are observed in (BEDO-TTF)$_2$ReO$_4$(H$_2$O) corresponding very well with two cross-sectional areas of the Fermi surfaces obtained for a hole and an electron pocket from tight binding calculations. In contrast, in κ-(BEDT-TTF)$_2$I$_3$ two relatively large closed sections (13% and 85% of the first Brillouin zone) of the Fermi surfaces are observed, again confirming the tight binding calculations. For κ-(BEDT-TTF)$_2$I$_3$ in magnetic fields above 12 T the effective mass for the larger orbit, as obtained from the temperature dependence of the SdH-oscillation amplitudes, is magnetic field dependent as long as the field is arranged perpendicular to the conducting planes ($\Theta = 0°$). In contrast, from dHvA measurements — which were performed by turning the magnetic field by 27° with respect to the SdH experiments — the observed effective mass is field independent. We suppose that the occurrence of anyons at temperatures below 1 K and in fields above 12 T might be the reason for the observed field dependence of the effective mass in the SdH investigations under the special angle 0°.

PACS numbers: 74.70.Kn, 71.25.Hc, 71.25.Jd

1. Introduction

Radical salts of the electron donors BEDT-TTF (bis-(ethylenedithiolo)-tetrathiafulvalene) and BEDO-TTF (bis-(ethylenedioxy)-tetrathiafulvalene) are usually quasi two-dimensional metals. $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ [1, 2] and κ-$(BEDT\text{-}TTF)_2I_3$ [3, 4] are two extreme cases of such two-dimensional electronic systems. On the other hand, two-dimensional (2D) electronic systems are of special interest due to the fact that in two space dimensions a continuous family of quasi-particles with quantum statistics interpolating between bosons and fermions might exist [5]. Experimental evidence for quasi-particles in two dimensions with such fractional statistics (anyons) were found in quantum Hall effect measurements, while the experiments searching for anyons in the case of the high temperature copper oxide superconductors are contradictory. In the case of the fractional quantum Hall effect the experiments were carried out on semiconducting heterostructures in the quantum limit in high magnetic fields (B) at low temperatures where $\omega_0\tau \gg 1$, with $\omega_0 = eB/m_0$ being the cyclotron frequency, τ — the electronic scattering time and m_0 — the free electron mass. Similar experimental conditions are fulfilled during SdH and dHvA investigations of the Fermi surfaces (FS) and effective masses in 2D organic superconductors. Since quasi-particles with fractional statistics occur under conditions where correlations are important, a magnetic field dependent effective mass might be observed in such cases.

In the present work, we have investigated the FS and effective masses of the two organic superconductors, $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ and κ-$(BEDT\text{-}TTF)_2I_3$. The calculated Fermi surfaces [2, 3] of both materials are extreme cases of 2D electronic systems. It was shown [2] that in the case of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ two closed pockets of the size of only about 1.5% and 3% of the first Brillouin zone (FBZ) exist (see Fig. 1a), where the first pocket belongs to electrons and the second to holes (showing that $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ is a semimetal), while in the case of κ-$(BEDT\text{-}TTF)_2I_3$ an elliptical hole orbit around Z of about 13% of the FBZ and a nearly circular hole orbit around Γ of about 85% of the FBZ exist (see Fig. 1b) [3, 6]. In addition for κ-$(BEDT\text{-}TTF)_2I_3$ it was shown that the FS has a nearly perfect cylindrical form with a negligible amount of warping [6].

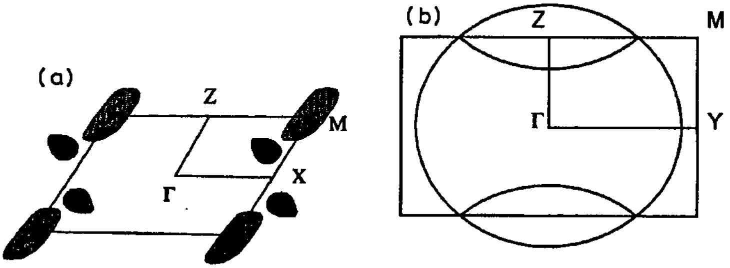

Fig. 1. (a) Hole and electron Fermi surface of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ [2], (b) Fermi surface of κ-$(BEDT\text{-}TTF)_2I_3$ [3].

Additional proof for the extreme 2D electronic behavior of κ-$(BEDT\text{-}TTF)_2I_3$ was obtained from measurements of the angular dependence of the upper critical field B_{c2}, which can be described perfectly by the Tinkham formula for 2D thin films and the mass anisotropy from the ratio of the critical fields $B_{c2\parallel}$ and $B_{c2|}$ was estimated to be at least $m_{\parallel}/m_{|} \approx 1/1500$ [6c].

2. Experimental

SdH and dHvA measurements were done in the High Field Laboratory of the Max Planck Institut in Grenoble, in magnetic fields up to 27 T and in the temperature range 0.4–4.2 K. The crystals were mounted in a holder such that they could be tilted during the experiment (in the case of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ around their a^*- and c-axis, the initial field orientation always being along the b-axis, while in the case of κ-$(BEDT\text{-}TTF)_2I_3$ the crystals could be tilted around their b- and c-axis, the initial field orientation always being along the a^*-axis, normal to the conducting bc-plane). The resistivity measurements were carried out by the usual four point method. For crystals of κ-$(BEDT\text{-}TTF)_2I_3$ dHvA experiments were performed in the usual torque arrangement. In order to obtain sufficient large dHvA signals, the magnetic field was turned by 27° out of the direction perpendicular to the conducting planes. In these cases the obtained $m^*(\Theta = 27^\circ)$ had to be multiplied by $\cos 27^\circ = 0.891$ in order to obtain the value $m^*(\Theta = 0^\circ)$. For the value of the effective mass at 25 T the magnetic field was turned only by 9°.

3. $(BEDO\text{-}TTF)_2ReO_4(H_2O)$

3.1. Results

Figure 2 shows SdH oscillations for a crystal of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ at 0.5 K versus the reciprocal magnetic field (for the range 6–24 T). Here the nonoscillating part of the resistivity was subtracted. The magnetoresistance behavior of a crystal of $(BEDO\text{-}TTF)_2ReO_4(H_2O)$ in the same field range (6–24 T) at several temperatures is shown in Fig. 3. At low temperatures the oscillation amplitudes at high magnetic fields is about 30% of the nonoscillating part of the resistivity. The Fourier analysis of the digitally stored quantum oscillations shows that there exist two fundamental frequencies $F_1 = (37 \pm 3)$ T and $F_2 = (76 \pm 2)$ T.

Those two frequencies correspond very well with two extremal cross-section areas $A_j = (4\pi^2 e/h)F_j$ of the FS with $A_1 = 0.35$ nm^{-2} and $A_2 = 0.75$ nm^{-2} representing two closed pockets of the size of about 0.7% and 1.5% of the cross-section of the FBZ. A more precise value of the frequency $F_2 = (75.0 \pm 0.3)$ T was obtained by linear regression from a plot of the number of Landau levels versus the reciprocal magnetic field (at 24 T there are still three Landau levels lying below the Fermi energy).

The fast Fourier transformation amplitudes of the SdH oscillations with the frequencies F_1 and F_2 were measured at eleven different temperatures in the field region between 6 T and 24 T. The temperature dependence of the amplitude was fitted to the temperature damping factor R_T of the Lifshitz–Kosevich (LK) formula

$$R_T = rz/\sinh(rz) \quad \text{with} \quad z = \lambda m^* T/m_0 B, \tag{1}$$

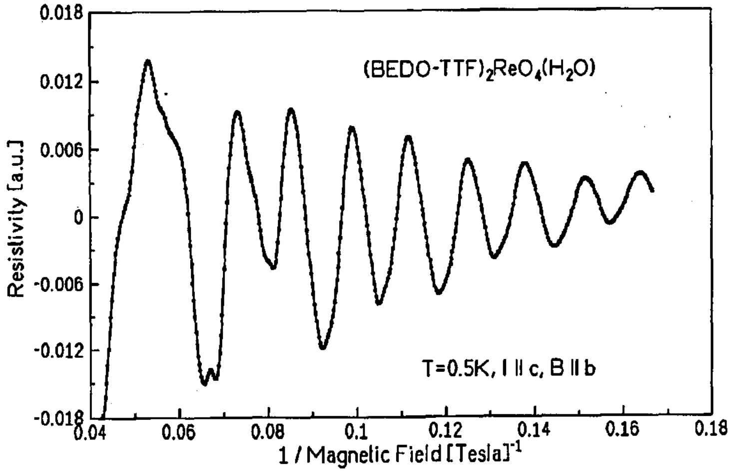

Fig. 2. SdH oscillations of single crystals of (BEDO-TTF)$_2$ReO$_4$(H$_2$O) at 0.5 K versus the reciprocal magnetic field for the field range 6–24 tesla.

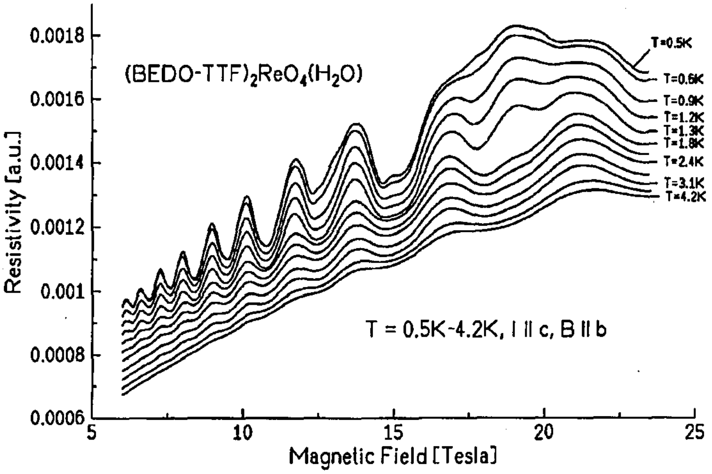

Fig. 3. SdH oscillations for a crystal of (BEDO-TTF)$_2$ReO$_4$(H$_2$O) in the field range 6 to 24 tesla at several different temperatures.

where $\lambda = \pi m_0 k_B / eh = 14.693$ T/K, m^* is the cyclotron effective mass and r is the number of the SdH harmonic ($r = 1$ for the fundamental). For the larger orbit (corresponding to the frequency F_2) this method yields $m^* = (0.90 \pm 0.05)m_0$. The effective mass for this larger orbit was also calculated from the oscillation amplitude of F_2 for a fixed magnetic field of 13.5 T and $m^* = 0.9m_0$ was found as well. For the smaller orbit $m^* = (1.15 \pm 0.1)m_0$ was obtained from the amplitudes of the Fourier transforms.

In order to study the geometry of the FS in more detail, SdH measurements were performed for various angles of inclination Θ between B and the b-axis. The SdH signal was observed in the field range from 6 T to 24 T at 0.5 K. Both oscillations could be observed at angles up to 80°. Figure 4 shows the measured angular dependence of the SdH frequencies F_1 and F_2 for B perpendicular to the c-direction. The data for both frequencies perfectly follow the behavior $F(\Theta) = F(0°)/\cos\Theta$, shown by the solid line, as expected for a cylindrical FS of a 2D electronic system.

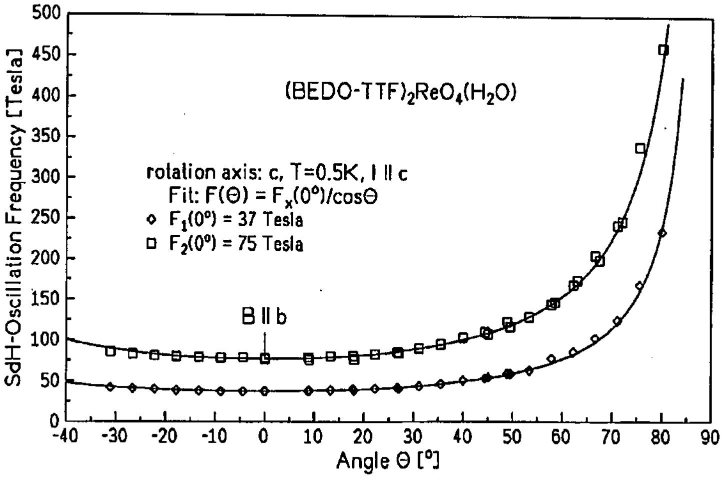

Fig. 4. Angular dependence of the SdH frequencies F_1 and F_2 for crystals of $(\mathrm{BEDO\text{-}TTF})_2\mathrm{ReO}_4(\mathrm{H}_2\mathrm{O})$. Solid lines: $F(\Theta) = F(0°)/\cos\Theta$.

3.2. Discussion

An important result of our investigations is the fact that the SdH measurements below 4.2 K showed that the FS of $(\mathrm{BEDO\text{-}TTF})_2\mathrm{ReO}_4(\mathrm{H}_2\mathrm{O})$ has two kinds of closed pockets in excellent agreement with the FS calculated on the basis of the room temperature crystal structure [2]. The fact that the experimentally observed sizes of the two pockets are about a factor of two smaller as the calculated ones is not surprising, since the crystals of $(\mathrm{BEDO\text{-}TTF})_2\mathrm{ReO}_4(\mathrm{H}_2\mathrm{O})$ undergo at least two phase transitions by cooling down to 4.2 K [1, 2].

The characteristic $1/\cos\Theta$ behavior of the SdH frequencies F_1 and F_2 shows that the FS has a perfect cylindrical shape as expected for such a 2D electronic system. In view of the small sizes of the closed pockets of only 1.5% and 0.7% of the FBZ, the observed cyclotron effective masses are relatively large. Effective masses of carriers observed for such small pockets are usually much smaller [7]. Therefore, in $(\mathrm{BEDO\text{-}TTF})_2\mathrm{ReO}_4(\mathrm{H}_2\mathrm{O})$ many-body interactions might give rise to an effective mass enhancement, but due to the relatively low frequencies of the quantum oscillations it is not possible to observe a magnetic field dependence of the effective masses, although at 24 T the system is already close to the quantum limit.

4. κ-(BEDT-TTF)$_2$I$_3$

4.1. Results

On several single crystals of κ-(BEDT-TTF)$_2$I$_3$ SdH and dHvA experiments were carried out in magnetic fields up to 27 tesla. Figure 5 shows typical dHvA and SdH oscillations of a single crystal of κ-(BEDT-TTF)$_2$I$_3$ (I) at 0.4 K versus the reciprocal magnetic field for the field range 10 to 24 tesla. Giant quantum oscillations can be seen in both types of experiments.

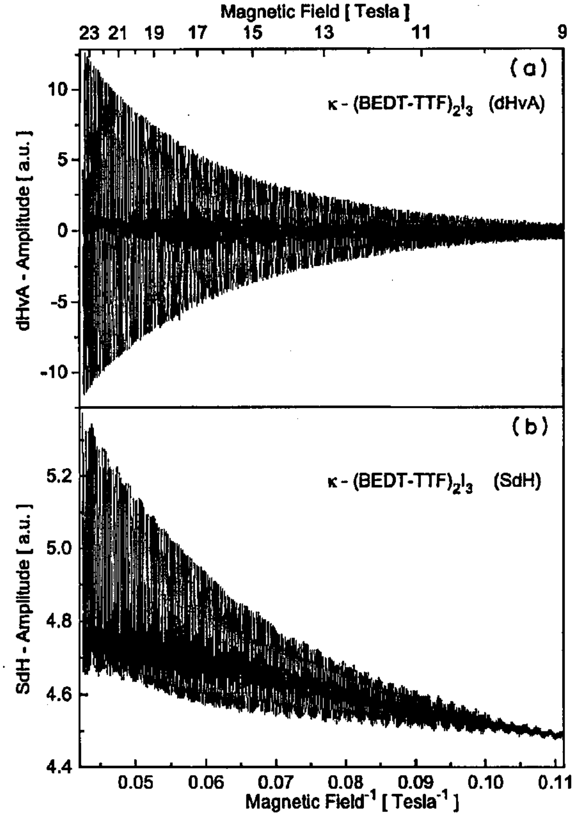

Fig. 5. (a) dHvA oscillations and (b) SdH oscillations of a single crystal of κ-(BEDT-TTF)$_2$I$_3$ at 0.4 K versus the reciprocal magnetic field.

Figure 6a shows SdH oscillations of another crystal of κ-(BEDT-TTF)$_2$I$_3$ (II) in the low field range from 3.5 to 7 T and Fig. 6b the oscillations in the high field range from 23 to 27 T. The main difference between both crystals I and II is that the Dingle temperature T_D for the higher frequency F_2 — as obtained from the magnetic field dependence of the oscillation amplitudes and the Dingle damping factor of the LK-formula — is 0.8 K for crystal I and only 0.4 K for crystal II.

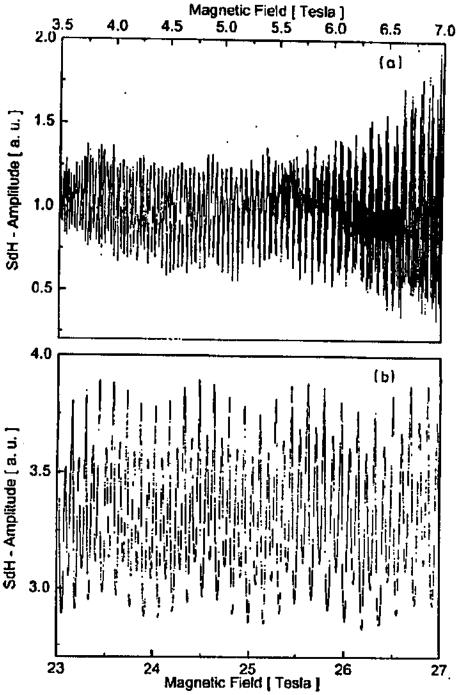

Fig. 6. (a) SdH oscillations of a crystal of κ-(BEDT-TTF)$_2$I$_3$ (II) for the field range 3.5 to 7 T (here the nonoscillating part of the magnetoresistance is subtracted) and (b) for the field range 23 to 27 T at 0.5 K.

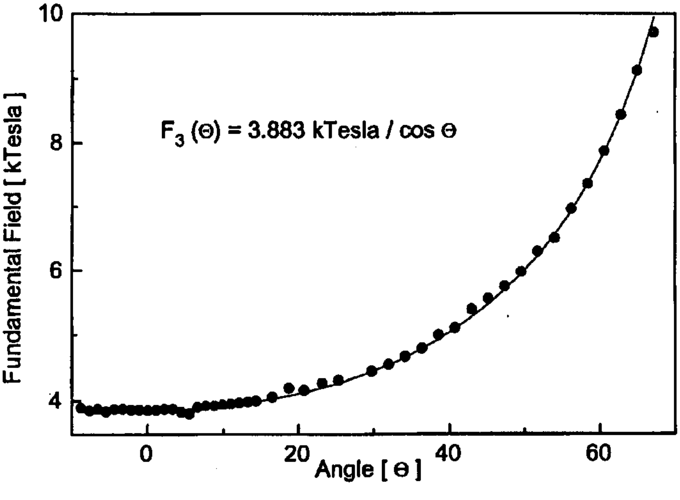

Fig. 7. Angular dependence of the SdH frequency F_2 of κ-(BEDT-TTF)$_2$I$_3$ ($\Theta = 0°$ means $\boldsymbol{B} \parallel a^*$) at 22.5 T. Solid line: $F(\Theta) = F(0°)/\cos\Theta$.

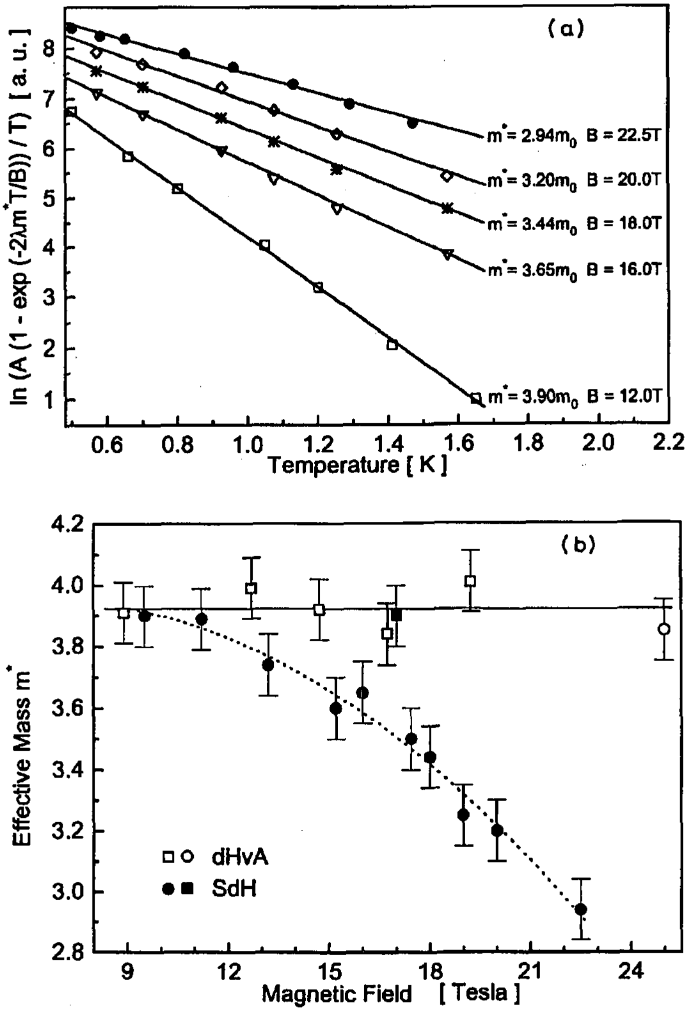

Fig. 8. (a) Temperature dependence of the SdH amplitudes of κ-(BEDT-TTF)$_2$I$_3$ of the frequency F_2 at several magnetic fields (crystal I). (b) Effective masses m^* for the larger orbit (F_2) of the FS of κ-(BEDT-TTF)$_2$I$_3$, as obtained from the temperature dependence of the SdH and dHvA oscillation amplitudes (see text).

The Fourier analysis of the digitally stored quantum oscillations reveals that there exist two fundamental frequencies $F_1 = (575 \pm 25)$ tesla and $F_2 = (3879 \pm 20)$ tesla which both correspond very well to the cross-sectional areas of the FS (see Fig. 1b) expected from a tight binding calculation [3].

In order to study the geometry of the FS in more detail, SdH measurements were performed for various angles Θ at a magnetic field of 22.5 T (an analogous study for the frequency F_2 and the effective mass m^* was performed from dHvA oscillations at 12 T [6a]). Figure 7 shows the measured angular dependence of the SdH frequency F_2. In all cases the data follow the behavior $F(\Theta) = F(0^\circ)/\cos\Theta$ (respectively $m(\Theta) = m(0^\circ)/\cos\Theta$ at 12 tesla!), shown by the solid line, as expected for a cylindrical FS of a 2D electronic system.

From the dHvA ($\Theta = 27^\circ$) and the SdH ($\Theta = 0^\circ$) experiments on crystal I the effective masses at several different magnetic fields were determined from the temperature dependence of the oscillation amplitudes using the LK-formula (see ordinate of Fig. 8a). In addition, one value of m^* was determined from an SdH experiment at about 17 T under an angle $\Theta = 9^\circ$ and one m^* value at 25 T from a dHvA experiment on crystal II under an angle $\Theta = 9^\circ$ as well.

Figure 8b shows the effective masses m^* versus the magnetic field for both types of experiments. An additional value of m^* for an SdH experiment at 25 T and $\Theta = 0^\circ$ is not included in this graphics since the obtained value was too small for this diagram in Fig. 8b, but in addition the obtained fit in analogy to Fig. 8a was very poor and the obtained value for m^* was afflicted with a large error.

4.2. Discussion

The angular dependence of the oscillation frequency F_2 (see Fig. 7) and of the corresponding effective mass m^* at 12 tesla (see Ref. [6a]) demonstrates the 2D character of the electronic system. Furthermore, from dHvA experiments at 12 T [6a] and measurements of the specific heat [8] it was shown that up to 12 T the FS of κ-(BEDT-TTF)$_2$I$_3$ can be very well described by the 2D free electron model. On the other hand, it is surprising that for the magnetic field perpendicular to the conducting planes ($\Theta = 0^\circ$) in fields above 12 T the effective mass m^* as obtained from the SdH oscillation amplitudes by the LK-formula continuously decreases with increasing magnetic field indicating correlation effects.

In contrast from dHvA experiments at $\Theta = 27^\circ$ and $\Theta = 9^\circ$ (as well as from the SdH experiment at $\Theta = 9^\circ$ and 17 T) in the whole field range from 12 to 27 tesla a magnetic field independent $m^*(0^\circ) = m^*(\Theta)\cos\Theta = 3.9m_0$ is obtained (the same value as from SdH and dHvA measurements below 12 T). In dHvA experiments the magnetic field is turned by 27° (at 25 T and in the SdH experiment at 17 T only by 9°) with respect to the SdH experiments at $\Theta = 0^\circ$, resulting in cyclotron orbits which cross several conducting planes (at 25 T and $\Theta = 9^\circ$ at least 10 planes). That means, we have a typical movement of electrons (or holes; in the following part we will talk only of electrons) in three dimensions.

In contrast in the SdH experiments at $\Theta = 0^\circ$, where a magnetic field dependent effective mass is observed, the magnetic field is perfectly arranged perpendicular to the conducting planes. In those experiments the cyclotron orbit lies exactly within the conducting *bc*-planes and the electrons have not to leave the individual plane to which they belong. Furthermore, in those experiments at temperatures below 1 K, the resulting kinetic energy of the electrons in the direction perpendicular to the conducting planes due to k_BT is too small in order to be able to leave the individual plane (within $\tau = 1/\omega_c$). In fact, under those conditions we investigate a 2D electronic system under broken time-reversal symmetry and broken parity, so that all the conditions for the occurrence of anyons are fulfilled.

Therefore, we suppose that under the conditions of the SdH experiments at $\Theta = 0^\circ$ above 12 T and below 1 K the observed magnetic field dependence of the effective mass is a sign for the occurrence of anyons, the quasi-particles which can exist only in a 2D electronic system. Since on the other hand, at 22.5 T the angular dependence of the oscillation frequency F_2 still follows perfectly the $(1/\cos\Theta)$-law — as expected for a cylindrical FS of a 2D electronic system — we suppose that in all experiments we observe a 2D electronic system, that means fermions, and even at $\Theta = 0^\circ$ we do not directly observe anyons. Instead, due to the occurrence of anyons the quantum oscillation amplitudes decrease and therefore from the fit of the experimental data to the LK-formula (see Fig. 8a) smaller effective masses seem to occur. In fact, those obtained effective masses are not the real effective masses, because the LK-formula (1), which is valid only for electronic systems with a constant number of fermions, cannot be used here for the determination of the effective mass in contrast to the dHvA and SdH experiments at angles $\Theta \neq 0^\circ$.

If in the SdH experiments at $\Theta = 0^\circ$ the occurrence of anyons is really the reason for the apparent observed field dependence of the effective mass, then we can state that here the occurrence of anyons is observed under similar conditions as in the fractional quantum Hall effect, i.e. only at relatively high magnetic fields (here above 12 T) and very low temperatures (below 1 K) when the electrons (holes) are forced to stay in their individual planes due to the special cyclotron orbit. This would also mean that the observed superconductivity in crystals of κ-(BEDT-TTF)$_2$I$_3$ at 4 K in zero magnetic field is *not* due to anyons.

Nevertheless, there are also differences with respect to the experiments of the fractional quantum Hall effect. In these experiments we are far away from the quantum limit (at 27 T still about 140 Landau levels lie below the Fermi level [9]) and we have many parallel layered conducting planes in the sample. Therefore, all kinds of quasi-particles belonging to a continuous family of quantum statistics, interpolating between bosons and fermions, might exist in our experiment. In order to prove the hypothesis of the occurrence of quasi-particles with fractional statistics in the quantum oscillation experiments under an angle $\Theta = 0^\circ$ further experiments are necessary and under progress. In addition, there might exist other organic metals with such extreme 2D electronic Fermi surfaces where similar experiments can be done (at least in β_H-(BEDT-TTF)$_2$I$_3$ similar conditions as in κ-(BEDT-TTF)$_2$I$_3$ exist) in order to search for anyons.

Acknowledgments

Very stimulating and valuable discussions with Professors Yu.A. Bychkov, A.M. Kosevich, T. Maniv, I. Wagner, M. Weger and Dr. J. Wosnitza are gratefully acknowledged. This work was supported by the Deutsche Forschungsgemeinschaft, the Forschungsschwerpunkt Supraleitung des Landes Baden-Württemberg and by the Commission of the European Communities [contract CI-CT 90-0863 (CD)].

References

[1] S. Kahlich, D. Schweitzer, I. Heinen, Song En Lan, B. Nuber, H.J. Keller, K. Winzer, H.W. Helberg, *Solid State Commun.* **80**, 191 (1991).

[2] S. Kahlich, D. Schweitzer, C. Rovira, J.A. Paradis, M.-H. Whangboo, I. Heinen, H.J. Keller, B. Nuber, P. Bele, H. Brunner, R.P. Shibaeva, *Z. Phys. B* **94**, 39 (1994).

[3] K. Kajita, Y. Nishio, S. Moriyama, W. Sasaki, R. Kato, H. Kobayashi, A. Kobayashi, *Solid State Commun.* **64**, 1279 (1987).

[4] E. Balthes, A. Breining, S. Kahlich, J. Moldenhauer, D. Schweitzer, P. Bele, H. Brunner, I. Heinen, B. Nuber, H.J. Keller, *Synth. Met.* **56**, 2859 (1993).

[5] F. Wilczek, *Phys. Rev. Lett.* **49**, 957 (1982).

[6] (a) M. Heinecke, K. Winzer, D. Schweitzer, *Z. Phys. B* **93**, 45 (1993); (b) E. Balthes, D. Schweitzer, I. Heinen, H.J. Keller, W. Biberacher, A.G.M. Jansen, E. Steep, Verh. der DPG, Münster 1994, p. 1665; (c) J. Wosnitza, N. Herrmann, X. Liu, D. Schweitzer, *Synth. Met.*, in print.

[7] D. Shoenberg, *Magnetic Oscillations in Metals*, Cambridge University Press, Cambridge 1984.

[8] J. Wosnitza, X. Liu, D. Schweitzer, H.J. Keller, *Phys. Rev. B*, in print.

[9] D. Schweitzer, E. Balthes, S. Kahlich, I. Heinen, H.J. Keller, W. Strunz, W. Biberacher, A.G.M. Jansen, E. Steep, *Synth. Met.*, in print.