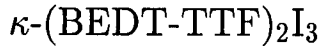


Proceedings of the IV International Seminar on Organic Materials for Molecular Electronics,
Zajaczkowo 1994

MAGNETIC FIELD DEPENDENT EFFECTIVE MASS IN THE ORGANIC SUPERCONDUCTOR



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$\kappa\text{-(BEDT-TTF)}_2\text{I}_3$ is an electronically extreme two-dimensional organic metal with a superconducting transition at around 4 K. In magnetic fields above 12 T the effective mass, as obtained from the temperature dependence of the amplitudes of Shubnikov-de Haas oscillations, is magnetic field dependent as long as the magnetic field is arranged perpendicular to the conducting planes. In contrast to this, by turning the magnetic field by 27° or even only 9° the observed effective mass (as obtained from Shubnikov-de Haas and de Haas-van Alphen measurements) is field independent. We suppose that the occurrence of anyons at temperatures below 1 K in fields above 12 T is the reason for the observed field dependence of the effective mass.

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

1. Introduction

The highest superconducting transition temperatures (T_c) in the class of the organic superconductors are observed in the so-called κ -phases of radical salts of the donor BEDT-TTF [bis-(ethylenedithiolo)-tetrathiafulvalene]. Here, among the ambient pressure superconductors, $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ possesses the second highest T_c of 10.4 K [1] and $\kappa\text{-(BEDT-TTF)}_2\text{CuN(CN)}_2\text{Br}$ the highest T_c of 12.2 K [2]. In those κ -phases the donor molecules are arranged in sheets and form face-to-face orthogonal dimers. There are two dimers per unit cell, related to each other by a 2_1 screw rotation. Taken by itself, without the anions, the donor layer is essentially centrosymmetric. The donor molecule packing in $\kappa\text{-(BEDT-TTF)}_2\text{I}_3$ ($T_c \approx 4.0$ K) [3, 4] is very similar with respect to

κ -(BEDT-TTF)₂Cu(NCS)₂, however, the space group is centrosymmetric ($P2_1/c$), allowing the I₃ anions to be located on inversion centers. Due to the centrosymmetric space group of κ -(BEDT-TTF)₂I₃ there exists a difference in the Fermi surface with respect to κ -(BEDT-TTF)₂Cu(NCS)₂. Using a tight binding extended Hückel method the band structures and Fermi surfaces of κ -(BEDT-TTF)₂Cu(NCS)₂ and κ -(BEDT-TTF)₂I₃ [5, 3] were calculated and in the case of κ -(BEDT-TTF)₂I₃ two conduction bands are found which are degenerated along the Z - M zone boundary, leading to nearly circular hole orbits around Z and around Γ (see Fig. 1 insert). In κ -(BEDT-TTF)₂Cu(NCS)₂ two bands cross the Fermi level as well, but the degeneracy is removed and the corresponding orbit around Γ now is open. In fact, those details of the Fermi surfaces were observed by Shubnikov-de Haas (SdH) and de Haas-van Alphen (dHvA) measurements [6, 7]. While in κ -(BEDT-TTF)₂Cu(NCS)₂ in low magnetic fields only one oscillation frequency in the SdH and dHvA measurements is observed and the orbit around Γ occurs only as a magnetic breakdown effect in fields above 15 T [7], in the SdH and dHvA measurements of κ -(BEDT-TTF)₂I₃ [6] two oscillation frequencies (at $F_1 = 575$ T and $F_2 = 3879$ T) are observable. In cases where the applied magnetic field is arranged perpendicular to the conducting planes in κ -(BEDT-TTF)₂I₃, from the temperature dependence of the SdH and dHvA oscillation amplitudes constant values for the effective mass in the magnetic field range between 6 T and 12 T were found ($m^* = 3.9m_0$).

The large oscillation amplitude of F_2 at fields above 9 T over a considerable temperature range allows the determination of the effective mass with high accuracy so that it is possible to find out whether m^* is magnetic field dependent or not. A magnetic field dependent effective mass might be observed in cases where the conventional independent particle mass is enhanced due to many-body interactions such as electron-phonon or electron-electron interactions. In the electronically extreme 2D system κ -(BEDT-TTF)₂I₃ (see Refs. [4, 7 and 9]) other typical 2D phenomena such as the occurrence of anyons at low temperatures and in very high magnetic fields might lead to a magnetic field dependent effective mass as well.

2. Experimental

κ -(BEDT-TTF)₂I₃ was first prepared by Kajita et al. [3]. In their preparation mixed electrolytes of $(n\text{-C}_4\text{H}_9)_4\text{NI}_3$ and $(n\text{-C}_4\text{H}_9)_4\text{NAuI}_2$ were used, resulting in crystals of κ -(BEDT-TTF)₂(I₃)_{1-x}(AuI₂)_x ($x \approx 0.006$). In our preparation, which was similar as reported for α -phase crystals [8], we used only the $(n\text{-C}_4\text{H}_9)_4\text{NI}_3$ salt in order to obtain pure, high quality single crystals of κ -(BEDT-TTF)₂I₃. The unit cell parameters for those monoclinic single crystals ($P2_1/c$) are: $a = 16.429$ Å, $b = 8.504$ Å, $c = 12.876$ Å, $\beta = 108.50^\circ$, $V = 1705.97$ Å³ and $R_w = 0.042$ (here we have used the same convention as in Refs. [3] and [7] in contrast to Ref. [4] where the space group $P2_1/a$ was employed). These parameters are slightly different from those obtained by Kajita et al. [3]. Crystals used in our experiments typically had dimensions of $2 \times 1 \times 0.5$ mm³ and superconducting transition temperatures of ≈ 4.0 K (measured by resistivity). The resistivity measurements were performed by the usual four-point method. SdH and dHvA measurements were done at the

High Field Laboratory of the Max Planck Institut in Grenoble, in magnetic fields up to 27 T and in the temperature range 0.4–1.3 K. The crystals were mounted in a holder so that they could be tilted (during the experiment) around their *b*- and *c*-axis, the initial field orientation being along the *a**-axis (normal to the *bc*-plane of conduction). The resistivity was always measured along the *c*-direction. The dHvA experiments were performed in the usual torque arrangement. In order to obtain sufficient large dHvA signals, the magnetic field had to be turned out of the direction perpendicular to the conducting planes by 27°. 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 $m^*(\theta = 0^\circ)$. At 25 T the magnetic field was turned only by 9°.

3. Results

On several single crystals of κ -(BEDT-TTF)₂I₃ SdH and dHvA experiments were performed in magnetic fields up to 27 T. Figure 1 shows typical dHvA and SdH oscillations obtained from those experiments. Giant quantum oscillations can

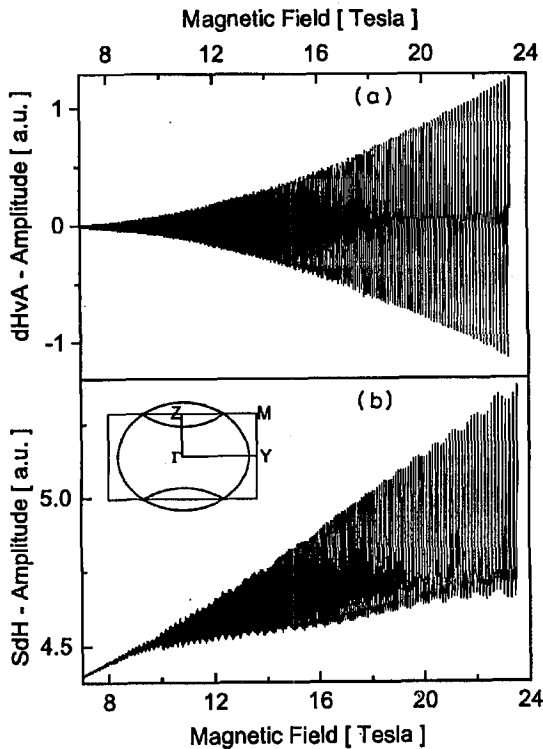


Fig. 1. (a) dHvA oscillations and (b) SdH oscillations of a single crystal of κ -(BEDT-TTF)₂I₃ at 0.4 K versus the magnetic field. Insert: Fermi surface of κ -(BEDT-TTF)₂I₃.

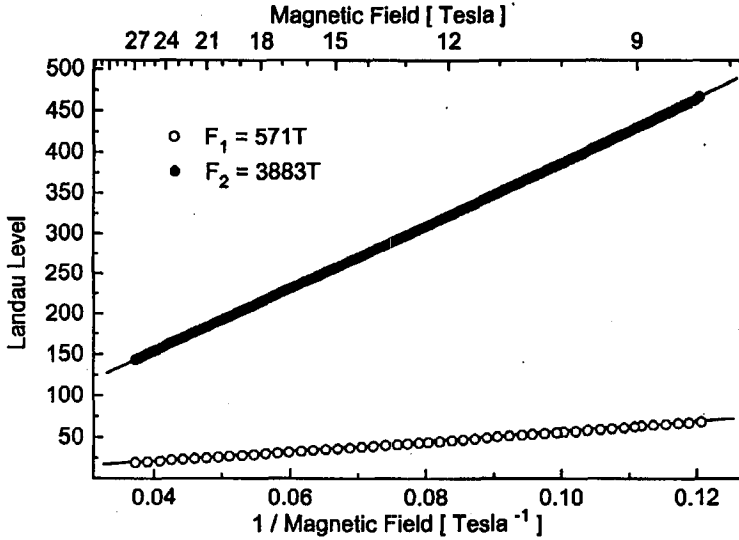


Fig. 2. Landau levels of both oscillation frequencies F_1 and F_2 of κ -(BEDT-TTF)₂I₃ versus the inverse magnetic field.

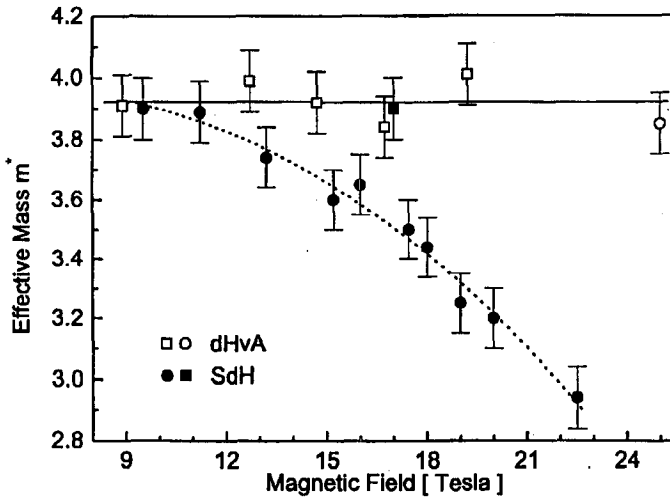


Fig. 3. Magnetic field dependence of the effective mass m^* for the larger orbit (F_2) of the Fermi surface of κ -(BEDT-TTF)₂I₃, as obtained from the temperature dependence of the SdH and dHvA oscillation amplitudes (see text).

be seen. At high magnetic fields the SdH oscillation amplitude is of the order of 20% with respect to the nonoscillating part of the magnetoresistivity. The insert in Fig. 2 shows the Fermi surface of κ -(BEDT-TTF)₂I₃ [3].

In Fig. 2 the number of the Landau levels (for F_1 and F_2) versus the reciprocal field $1/B$ for $\mathbf{B} \parallel \mathbf{a}^*$ is drawn. From the slope of the plots more precise values of $F_1 = 571$ T and $F_2 = 3883$ T are obtained. With the assumption of a circular Fermi surface, i.e. $\varepsilon_F = \hbar^2 A_k / 8\pi^3 m_0$, where ε_F is the Fermi energy and $A_{k=2} = 8\pi^3 e F_2 / h$ is the area of the Fermi surface corresponding to F_2 , the Sommerfeld coefficient for a 2D electron gas $\gamma = \pi^2 R k_B / 3\varepsilon_F = (20.5 \pm 0.5)$ mJ K⁻² mol⁻¹ is obtained in excellent agreement with a value of (18.9 ± 2) mJ K⁻² mol⁻¹ obtained by a specific heat measurement [9].

From the SdH and the dHvA experiments the effective masses at several magnetic fields were determined from the temperature dependence of the oscillation amplitudes using the Lifshitz–Kosevich formula. In addition one value of m^* was determined from an SdH experiment at about 17 T under an angle $\Theta = 9^\circ$. Figure 3 shows the effective masses obtained from both types of experiments.

4. Discussion

The angular dependence of the higher oscillation frequency as well as of the effective mass at 12 T (see Refs. [6a and 9]) perfectly follows the $(1/\cos \Theta)$ -law as expected for a cylindrical Fermi surface of a 2D electronic system. Furthermore, from dHvA experiments at 12 T and measurements of the specific heat [9] it was shown that up to 12 T κ -(BEDT-TTF)₂I₃ can be described very well by the 2D free electron model. Therefore, it is surprising that for $\Theta = 0^\circ$ in fields above 12 T the effective mass m^* continuously decreases with increasing magnetic field. In contrast from the dHvA experiments at $\Theta = 27^\circ$ and $\Theta = 9^\circ$ in the whole field range as well as from the SdH experiment at $\Theta = 9^\circ$ at 17 T a magnetic field independent $m^*(0^\circ) = 3.9m_0$ (the same value as from all measurements below 12 T) is obtained. Since dHvA experiments are made at $\Theta = 27^\circ$ and $\Theta = 9^\circ$, the electrons have to leave the individual conducting plane they belong to and cross several planes (at 25 T at least 10 planes) following their cyclotron orbits perpendicular to the direction of the magnetic field. In this case we detect the behavior of a 2D electronic system in three dimensions. In contrast in SdH experiments the magnetic field is arranged exactly perpendicular to the conducting planes so that the cyclotron orbits lie completely within the individual conducting planes. In this case we investigate a 2D electronic system under broken time-reversal symmetry and broken parity so that all the conditions for the occurrence of anyons [10], quasi-particles which can only exist in a 2D electronic system, are fulfilled. Since anyons do not obey Fermi statistics, we suppose that the occurrence of anyons leads to a decrease in the SdH oscillation amplitudes at high magnetic fields and temperatures below 1 K and therefore from the fit of the experimental data to the LK-formula smaller effective masses are obtained. In fact, those obtained effective masses are not the real effective masses, because the LK-formula, 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 $\Theta > 0^\circ$. Therefore, we do not directly observe the anyons in our experiment, but a decreasing SdH oscillation amplitudes due to the occurrence of anyons at $\Theta = 0^\circ$.

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)].

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