Materials Science-Poland, Vol. 22, No. 4, 2004

Quantum oscillation measurements on the organic superconductor Θ-(BEDT–TTF)$_2$I$_3$

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Quantum oscillation experiments were performed on high quality single crystals of Θ-(BEDT–TTF)$_2$I$_3$. Their electronic properties are similar to those of crystals of Θ-(BEDT–TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$ (x < 0.02). Nevertheless, in the neat crystals used here, quantum oscillations for the α-orbit (F_α= 780 T) are observed already at a field of 2 T, and the magnetic breakdown of the β-orbit (F_β = 4200 T) occurs at 3 T. In the large magnetic field range, in which quantum oscillations are observed, the warping of the Fermi surface of the α-orbit and β-orbit could be determined to be ΔF_α = 6.6 T and ΔF_β = 16.6 T, respectively. At high magnetic fields, the de Haas–van Alphen signal consists of pronounced inverse saw-tooth oscillations, and the Shubnikov–de Haas signal has a peaked structure. This behaviour is interpreted in terms of magnetic interaction.

Key words: *quantum oscillation*; *magnetic field; organic superconductors; Fermi surface*

1. Introduction

The electrochemical synthesis of I_3^- anions with radical salts of the electron donor BEDT–TTF (i.e., bis(ethylenedithio)tetrathiafulvalene) results in a number of electronically quasi-two dimensional (Q2D) organic metals with identical stoichiometry, namely (BEDT–TTF)$_2$I$_3$, but different structures. The usual synthesis produces mainly crystals of the so-called α- or β-phases, but also single crystals of the κ- or even Θ-phase may grow. Here we present quantum oscillation experiments on neat single crystals of Θ-(BEDT–TTF)$_2$I$_3$. In earlier investigations on crystals with a similar stoichiometry, Θ-(BEDT–TTF)$_2$(I$_3$)$_{1-x}$(AuI$_2$)$_x$ (x < 0.02) [1–7] it has been shown that

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those crystals are metallic down to low temperatures [1]. It has also been demonstrated [1, 2] that a part of the Θ-$(BEDT–TTF)_2(I_3)_{1–x}(AuI_2)_x$ ($x < 0.02$) crystals indeed become superconducting at 3.6 K, while others do not show a superconducting transition. The origin for this behaviour is not clear yet. The Fermi surface was investigated by Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) measurements. In high magnetic fields, the dHvA oscillations became saw-toothed [3], which was ascribed to an oscillating chemical potential in connection with strong two-dimensional electronic properties ($\rho_\perp/\rho_\parallel = 1000$) [4]. Our investigations on neat Θ-$(BEDT–TTF)_2I_3$ single crystals yield somewhat different results. It will be shown that the Fermi surface is warped and that besides "inverse saw-tooth" dHvA oscillations in high magnetic fields, peaky SdH oscillations are also observed. Both results are discussed in terms of the so-called magnetic interaction effect [8].

2. Experimental

Θ-$(BEDT–TTF)_2I_3$ crystals were synthesised electrochemically, however without adding AuI_2^- anions during the preparation as mentioned in previous reports [1, 5]. Some single crystals used in the experiments showed a steep superconducting transition, while others did not (see above). Quantum oscillation experiments were made in a ^{3}He cryostat (0.4 K), using a rotatable sample-holder. High magnetic fields on the superconducting magnets (up to 10 T) as well as on the resistive magnets (up to 28 T) were provided by the Grenoble High Magnetic Field Laboratory. DHvA experiments were carried out by the torque method [8], whereas for SdH measurements the single crystals were contacted by the "standard four probe method" using 25 μm gold wires and carbon paint. The current was applied normal to the highly conducting (a, b) plane*. In order to verify the reproducibility of the results, the SdH measurements were carried out simultaneously for several crystals on completely separated electronic setups.

3. Results

The crystal structure of neat Θ-$(BEDT–TTF)_2I_3$ crystals belongs to the monoclinic space group with $P2(1)/c$ symmetry. The lattice parameters are: $a = 9.926$ Å, $b = 10.074$ Å, $c = 34.201$ Å, $\beta = 98.27°$. The packing motive of the molecules and the structure data are very similar to those of Θ-$(BEDT–TTF)_2(I_3)_{1–x}(AuI_2)_x$ ($x < 0.02$) crystals [1], whereby most of the Θ-$(BEDT–TTF)_2(I_3)_{1–x}(AuI_2)_x$ ($x < 0.02$) crystals are twinned to form a pseudo-orthorhombic lattice with half of the length in the a-direction as compared to the monoclinic cell. Since most of the present neat

*The structure data of the monoclinic cell were used.

Θ-(BEDT–TTF)$_2$(I$_3$) crystals are not twinned, the frequencies of quantum oscillations as well as the warping of the Fermi surface could be determined very accurately.

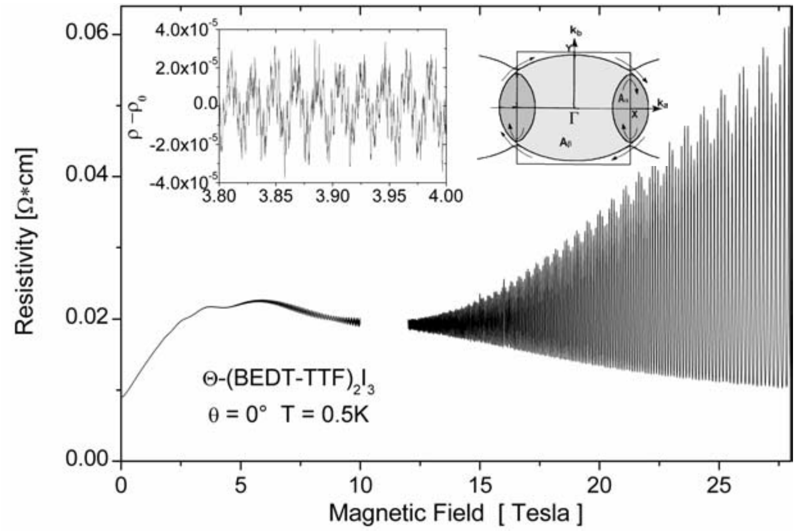
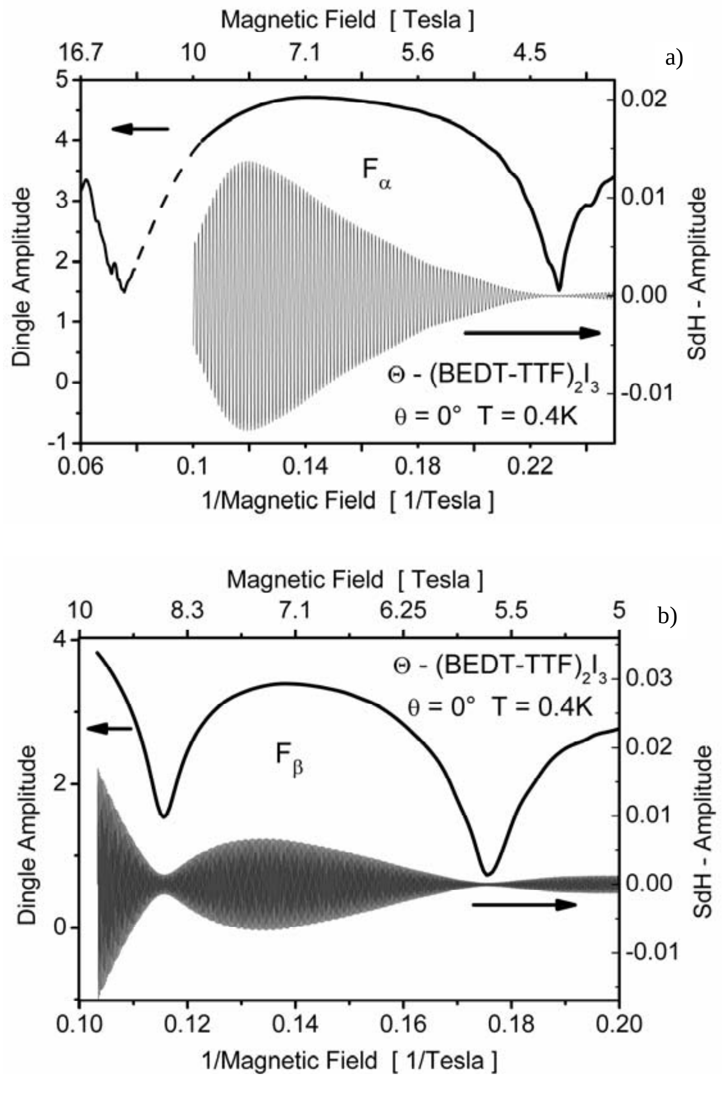


Fig. 1. Fermi surface and magneto-resistance of Θ-(BEDT–TTF)$_2$I$_3$ (see text). The inset shows the low-field part after subtracting the nonoscillatory background magneto-resistance

From the huge SdH oscillations shown in Fig. 1, the frequencies F_α = 780±10 T of the small α-orbit, F_β = 4200±20 T of the larger β-orbit (see the Fermi surface in Fig. 1), as well as F_γ = 7.8±0.2 T of the small three-dimensional (3D) orbit [3, 6] were determined (the orbit corresponding to F_γ is not shown on the Fermi surface). The inset in Fig. 1 shows the low-field SdH signal after subtracting the nonoscillatory background magnetoresistance. The angular dependences of the frequencies and the effective carrier masses (m_α = 1.8m$_0$ and m_β = 3.5m$_0$ at an angle of 0°; m_0 is a free electron mass) are obtained by declining the conducting planes out of the position perpendicular to the magnetic field (where $B \perp (a, b) \equiv \theta = 0°$). These properties show a $1/\cos\theta$ behaviour as expected from a Q2D electronic system.

Figure 2a, b shows the so-called Dingle plots of the α- as well as the β-orbit versus the inverse magnetic field, as well as the SdH oscillations after filtering the experimental data by a band-pass filter (for 780 T in Fig. 2a and 4200 T in Fig. 2b). Figure 2c shows the field range from 4 to 10 T and compares the raw data of the SdH experiment after subtracting the background (bottom) with the composed curve obtained from the filtered signals of Figs. 2a and b (top). The minima in the Dingle plots in Fig. 2a and b correspond to the minima (i.e., “beating nodes”) of the oscillation amplitudes. Therefore, a Dingle plot is a good way to determine these beating nodes. The beating nodes, however, can be observed in the oscillation curves as well, which were band-pass filtered. Figures 2a–c show the 1st and 2nd beating nodes of the α-frequency and the 2nd and 3rd nodes of the β-frequency. From the beating frequencies, $\Delta F_{\alpha} = 6.6$ T and $\Delta F_{\beta} = 16.6$ T, the warping (i.e., corrugation) of the Fermi surface is estimated to be 0.8% for the α-orbit and 0.4% for the β-orbit. The beating nodes of the β-frequency are at the theoretically predicted positions for beating in consequence of warping [9], whereas the beating nodes of the α-frequency are shifted, so that they occur at the positions: $B_n = \Delta F/(n + 1/4)$. A similar shift for beating nodes in SdH measurements was observed in $(BEDT–TTF)_4[Ni(dto)_2]$ crystals by Schiller et al. [10]. As soon as the crystal is declined to the magnetic field by an angle of 15° (which represents the first Yamaji angle, measured by Kajita et al. [2]), the beating of the β-frequency disappears. This confirms that the beating is created by a warping of the Fermi surface, but not by the assumed twinned structure of the crystal.



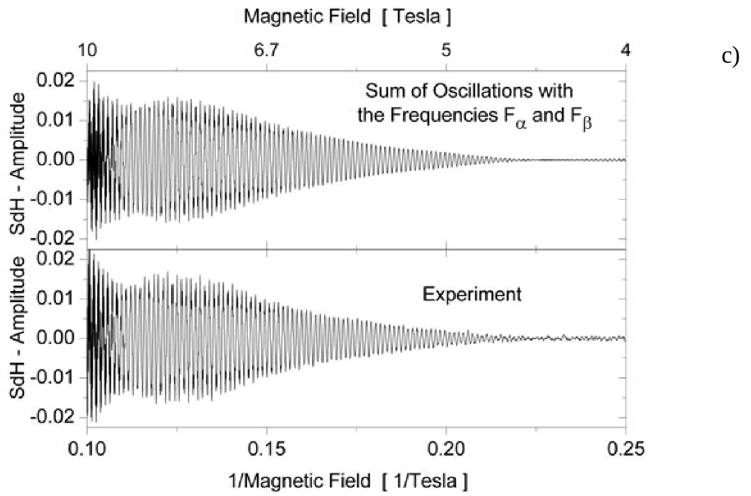


Fig. 2. Dingle plots of F_α (a) and F_β (b), and the detected SdH oscillations versus 1/B, after passing them through a band-pass filter, for 780 T (a) and 4200 T (b). Detected SdH oscillations versus 1/B (for 4 T ≤ B ≤ 10 T) after subtracting the background (c). For comparison (top): The composed signal, obtained from the filtered signals of (a) and (b)

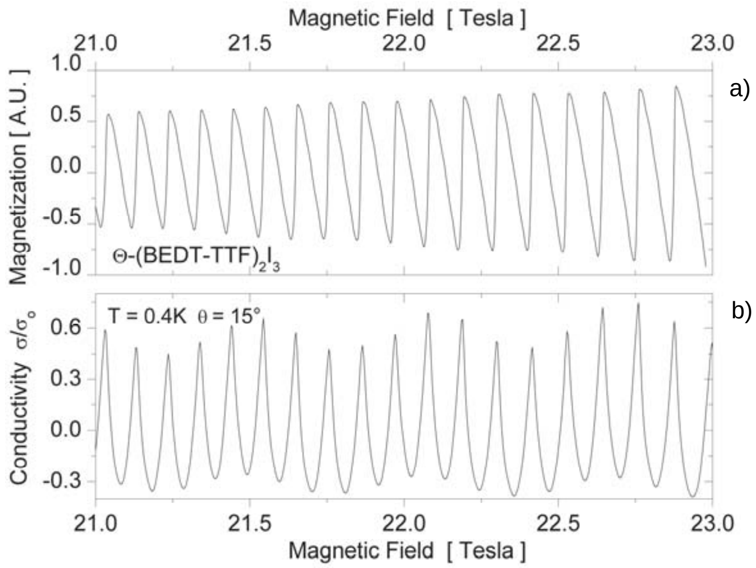


Fig. 3. Comparison of the shape of the oscillations in magnetization (a) and conductivity (b) at T = 0.4 K, θ = 15°, and high magnetic fields (see text for details)

Concerning the 3D γ-orbit (F_γ = 7.8 T) [6], it can be estimated from Fig. 1 that the last Landau cylinder passes the γ-orbit at a field of about 10 T (to be seen as a minimum in resistivity). The 3D γ-orbit has the shape of a cigar. The cross-section normal to the *b*-direction has a size of 0.018 nm^{-2} (1.9 T).

At high magnetic fields, the oscillations in magnetization (i.e., dHvA) show a so-called inverse saw-tooth shape for angles $15° \le \Theta \le 60°$, which means that the sheer flank is on its low-field side (see Fig. 3, top). Corresponding to this sharp saw-tooth signal, the fast Fourier transform (FFT) shows 18 harmonics of F_β (not shown here). A similar behaviour is observed in the SdH signal, where the conductivity should be identical to the derivative of the dHvA signal. In fact the magnetic field dependence of conductivity at high fields shows a peaky structure (shown in the bottom of Fig. 3), and the FFT also shows a rich harmonic content of F_β. Considering the above-mentioned relation between SdH and dHvA signals, it is important that the peaks in the SdH signal point *upwards*. This fact confirms that the shape of the dHvA signal is indeed an 'inverse' saw-tooth, instead of a 'normal' saw-tooth, which might be shifted by 180^o within the dHvA data detection process. The orientation of the saw-tooth is decisive for its interpretation (see below).

4. Discussion

The observed huge quantum oscillation amplitudes (see Fig. 1) indicate a high quality of the neat Θ-$(BEDT–TTF)_2I_3$ crystals. The observed frequencies are similar to those detected in Θ-$(BEDT–TTF)_2(I_3)_{1-x}(AuI_2)_x$ ($x < 0.02$). The so-called magnetic breakdown between the small α-orbit (F_α = 780 T) and β-orbit (F_β = 4200 T) was observed at a magnetic field of only 3 T at 0.4 K (and not at 15 T, as mentioned in the literature for Θ-$(BEDT–TTF)_2(I_3)_{1-x}(AuI_2)_x$ ($x < 0.02$) crystals [3]).

As pointed out above, the oscillations in magnetization (dHvA) show an inverse saw-tooth (see Fig. 3 top) at high magnetic fields. One origin of saw-tooth variations in the magnetization may be an oscillation of the chemical potential μ in a strong two-dimensional electronic system as a function of the magnetic field. For such a situation, two cases can be distinguished. At first, the 2D closed orbit in *k*-space (here corresponding to F_β) may be coupled to a further trajectory on the FS, to which the carrier tunnelling is possible. In this case, the latter trajectory would represent a reservoir for F_β, and in conclusion the orientation of the saw-tooth would be "inverse" as described above. In the second case (not given here), i.e. in the absence of such a reservoir, the orientation of the saw-tooth would be "normal", i.e. with its sheer flank on its high-field side [7, 8]. At a first glance, the orientation of the observed saw-tooth should hint the realisation of the former case, with the 3D γ-orbit as a candidate for such a reservoir. F_γ can probably be excluded as an electron reservoir, however, since F_γ is already present at low fields (1 T) and a magnetic breakdown between F_β and F_γ is not observed up to 10 T. This means that the energy gap(s) between the F_γ-orbit and the other 2D orbits (i.e., F_α and F_β) is (are) too large to enable carrier tunnelling. This excludes F_γ from being a reservoir. Therefore, the observed "inverse" saw-tooth dHvA oscillations must have a different explanation.

If the dHvA signal is so huge that the oscillatory magnetization itself modifies the effective internal field, the shape of oscillations may be turned to an inverse saw-tooth with its sheer flank on its low-field side [8]. Considering this, we assume that magnetic interaction is the dominant reason for the inverse saw-tooth signal at high magnetic fields in the dHvA-experiment for Θ-(BEDT–TTF)$_2$I$_3$, rather than the above-mentioned presence of a reservoir. The observed strong temperature dependence of the saw-tooth supports the interpretation proposed above. In addition, a paramagnetic behaviour was observed in this material at temperatures below 20 K and fields above 0.05 T by SQUID and ESR measurements [11], whereas the material showed poor metallic behaviour (and even diamagnetic behaviour due to superconductivity below 3.5 K) at lower fields. This feature might be a further indication of the presence of magnetic interaction in Θ-(BEDT–TTF)$_2$I$_3$ at high fields.

Acknowledgements

This work has been supported by the Human Potential Programme under contract N^o HPRI-1999-CT-00030 and the International Max-Planck Research School of the Max-Planck-Institutes Stuttgart, Germany.

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Received 14 September 2004
Revised 29 September 2004