On the stoichiometry of the organic metal bis(ethylenedioxy)-tetrathiafulvalene chloride

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Abstract. We report on Shubnikov–de Haas and de Haas–van Alphen measurements of an organic metal based on the molecular donor bis(ethylenedioxy)-tetrathiavulvalene (= BEDO-TTF) and the anion Cl^- with H_2O molecules. The observed single oscillation frequency perfectly follows the two-dimensional dependence $F = F_0/\cos\Theta$ with $F_0 = (4890 \pm 20)$ T. The Fermi-surface area of $\sim 50\%$ of the first Brillouin zone proves a quarter-filled band, *i.e.*, a 2:1 stoichiometry of the BEDO-TTF donor with respect to the anion. The apparent discrepancy to X-ray data which give a 1:1 ratio between BEDO-TTF and Cl^- is understood by replacement of H_2O molecules with $(H_3O)^+$ ions. The proposed stoichiometry therefore is $(BEDO\text{-}TTF)_2^+ (H_5O_2)^+ (Cl^-)_2$. The cyclotron effective mass is $m_c = (1.54 \pm 0.05)m_e/\cos\Theta$ when deduced from the temperature dependence of the fundamental oscillation amplitude, but strongly reduced when extracted from higher harmonics. This and the strong harmonic content of the oscillations signals an influence of the two-dimensional electronic structure and can be qualitatively understood by applying the concept of magnetic interaction to the effect of the oscillatory chemical potential.

PACS. 71.18.+y Fermi surface: calculations and measurements; effective mass, g factor – 71.20.Rv Polymers and organic compounds

1 Introduction

Since the discovery of superconductivity in low-dimensional organic metals large efforts have been spent on the search for new molecular building blocks which give rise to novel metallic and eventually superconducting materials. The largest number of organic superconductors with transition temperatures up to ~ 13 K have been found in charge-transfer salts based on the donor BEDT-TTF (= bis(ethylenedithio)-tetrathiafulvalene) [1]. One route in the search for new organic metals was the substitution of the outer sulfur atoms in BEDT-TTF by oxygen which eventually led to the isostructural donor molecule BEDO-TTF (= bis(ethylenedioxy)-tetrathiafulvalene) [2]. The reduced molecular weight of this molecule should increase the Debye temperature in BEDO-TTF based charge-transfer salts which in turn to first approximation should increase the superconducting transition temperature T_c according to BCS theory with electron-phonon coupling. Of course, this is only valid if identical crystal

structures for the BEDO-TTF and BEDT-TTF salts are assumed. Up to date, two BEDO-TTF based superconductors have been synthesized [3,4]. However, contrary to expectation the transition temperatures are relatively low around 1–2 K. The reason for these low T_cs and for the small number of superconductors found in BEDO-TTF salts is the formation of different crystal structures for the BEDO-TTF salts with respect to the BEDT-TTF analogues and possibly the strong structural disorder in many of these crystals. It is certainly of great interest to get a better knowledge of the electronic structures and properties of these quasi-two-dimensional organic metals based on the donor molecule BEDO-TTF.

One recently synthesized non-superconducting metal based on BEDO-TTF contains Cl^- anions and H_2O molecules [5]. A considerable discrepancy between the previously proposed composition based on X-ray diffraction data $(BEDO\text{-}TTF)^+ Cl^- (H_2O)_x$ [5], and the Fermi-surface data was realized [6,7]. The former data clearly show a stoichiometry of 1:1 between the BEDO-TTF donor and Cl. A charge transfer of one electron per BEDO-TTF molecule would result in a half-filled band for which extended Hückel tight-binding band-structure calculations [6] predict a Fermi-surface topology similar to that found

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in κ-phase salts [8] with a cross section equal to the first Brillouin zone. Salts with this composition and band filling usually show a lattice dimerization with a concomitant metal-insulator transition upon cooling. However, the temperature dependence of the resistivity shows metallic behavior down to lowest temperature and infrared measurements [9] show a charge distribution typical for a 2:1 salt. Direct determinations of the Fermi-surface cross section by Shubnikov–de Haas (SdH) and de Hass–van Alphen (dHvA) investigations showed oscillations which yield a value of approximately half the area of the first Brillouin zone [6]. This corresponds to a 2:1 composition with band filling of three quarter, namely a charge transfer of one electron per two BEDO-TTF molecules.

Because of this puzzling discrepancy we performed further SdH and dHvA experiments on high-quality single crystals. We obtain agreement with the results of Mori *et al.* [6], however, with a much better signal-to-noise ratio. This confirms the discrepancy with the X-ray data which definitely show that for one BEDO-TTF molecule only one Cl^- and one water molecule exist. Therefore, we propose a composition of $(BEDO\text{-}TTF)_2^+ (Cl^-)_2 (H_5O_2)^+$ which is in accord with both X-ray and quantum oscillation results.

In the previous experiments [6] only a weak SdH signal with node-like features and strongly anharmonic dHvA data were report. The former feature hints at a more three-dimensional modulated Fermi surface or, alternatively, at a twined sample. On the other hand, strong anharmonicities are expected for materials with a highly two-dimensional (2D) electronic structure if not caused by magnetic or torque interaction effects. However, the authors of [6] give no explanation nor a discussion of these controversial issues. In order to gain more information on the dimensionality of $(BEDO\text{-}TTF)_2Cl_2(H_5O_2)$ we investigated the angular dependence of the SdH and dHvA effect up to $\Theta = 60°$, where Θ is the angle between B and the normal to the BEDO-TTF planes. We find good agreement between SdH, torque dHvA, and modulation-field dHvA data. We discuss in more detail the effective cyclotron mass, spin-splitting zeros, and deviations from the conventional three-dimensional Lifshitz–Kosevich (LK) formula.

2 Experimental

The single crystals of $(BEDO\text{-}TTF)_2Cl_2(H_5O_2)$ were grown by electrocrystallization as described in detail earlier [10]. The black plate-like crystals had irregular shapes with maximum dimensions of 3×3 mm^2 within the plane and thicknesses of less than 100 μm. Often some of the single-crystalline plates were grown on top of each other. In order to achieve a better mechanical stability we used one of this intergrown samples for the SdH experiment. However, we tried to put the four contacts only on the top plane of one crystallite, thereby feeding the current mainly parallel to the ab plane which should reduce possible twinning effects. For the dHvA experiments we chose smaller and thinner crystals which optically seemed to be
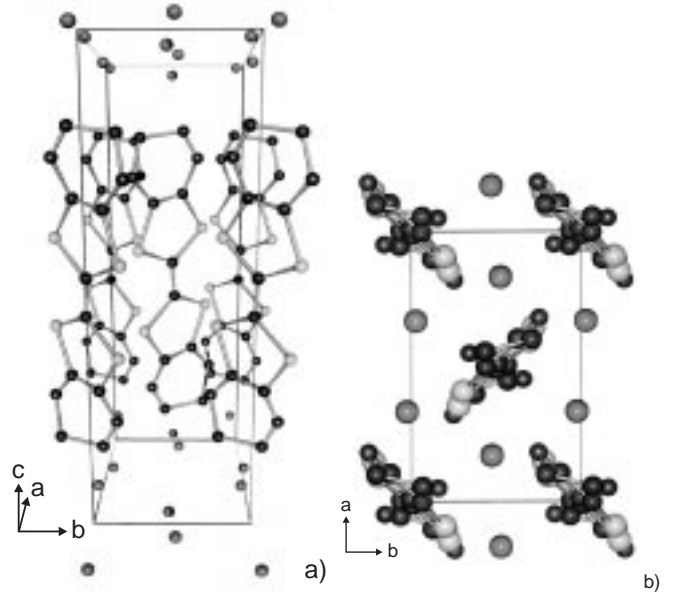

Fig. 1. Crystal structure of $(BEDO\text{-}TTF)_2Cl_2(H_5O_2)$ in a projection along the a axis (left) and along the $c^\star$ axis (right).

single crystalline. Due to the thermal stress caused by the vacuum grease to fix the sample the brittle crystals broke into parts as we realized after the measurements.

The torque dHvA measurements were performed in a ^{3}He cryostat ($T \geq 0.4$ K) in fields up to 28 T at the high-field laboratory in Grenoble. Two different samples (A and B) were measured. Details of the capacitance cantilever torquemeter are given in [11]. The SdH and modulation-field dHvA experiments were performed at Karlsruhe in a ^{3}He cryostat equipped with a 15 T superconducting magnet. The dHvA signal (sample C) was measured with a modulation field of frequency 780 Hz and amplitude ≤ 1 mT. The resistivity of sample D was measured with a commercial ac-resistance bridge with frequency 16 Hz. The residual resistivity ratio of sample D was about 100. In all experiments a rotational probe allowed the *in situ* rotation of the samples by more than 180° with an accuracy of better than 0.1°. In order to extract the SdH signal which is proportional to the relative conductance oscillations we calculated the conductance σ by inverting the resistance data, fitted the steady part of the conductance, σ_{steady}, by a polynomial, and calculated the relative conductance oscillations ($\sigma/\sigma_{steady} - 1$). All data analysis and Fourier transformations were applied to these conductance-oscillation data.

3 Results and discussion

The monoclinic crystal structure of $(BEDO\text{-}TTF)_2Cl_2(H_5O_2)$ is shown in Figure 1 for two different projections. The cell parameters can be found in [5]. The BEDO-TTF molecules form staples along b which lie side by side within the ab plane. The short distance between the donor molecules, which is less than the sum of the
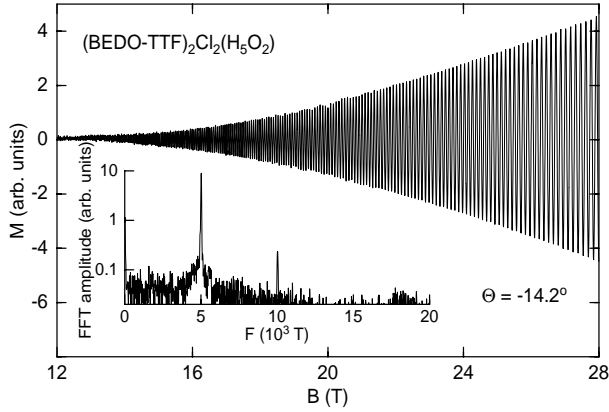
Fig. 2. Oscillating signal of the magnetization of (BEDO–TTF)$_2$Cl$_2$(H$_5$O$_2$) (sample A) measured by the torque method at an angle $\Theta = -14.2°$. The Fourier transformation of the data in the inset shows the spectral purity of the signal with a fundamental frequency of $F = 5020$ T and the second harmonic at $2F$.

Fig. 3. Shubnikov–de Haas signal of sample D at $\Theta = 5.5°$ (upper panel) and de Haas–van Alphen signal of sample C measured with modulation-field technique at $\Theta = -10.1°$ (lower panel). The insets show the Fourier transformations of the data.

van der Waals radii, assures almost isotropic transfer integrals within the ab plane and a corresponding simple 2D Fermi surface. Along c the donor planes are separated by insulating anion sheets. The crystallographic data show that Cl$^-$ anions and H$_2$O molecules statistically occupy two lattice sites with an occupation factor of 0.5 each.

Figure 2 shows the torque signal of sample A at $\Theta = -14.2°$ and $T = 0.4$ K between 12 and 28 T. Clear dHvA oscillations are visible over the whole field range. The Fourier transformation (inset of Fig. 2) reflects the spectral purity of the signal with only one fundamental frequency $F = 5020$ T and a small second harmonic at $2F = 10040$ T. SdH results (upper panel of Fig. 3) and dHvA oscillations obtained with the modulation-field method (lower panel of Fig. 3) are perfectly in line with the torque data. The SdH oscillations at $\Theta = 5.5°$ and $T = 0.47$ K have a frequency of $F = 4910$ T, the dHvA signal at $\Theta = -10.1°$ and $T = 0.45$ K has a frequency $F = 4980$ T. For all measurements only one fundamental frequency was found with the expected 2D behavior $F = F_0 / \cos \Theta$. Figure 4 shows the angular dependence of the dHvA frequency from the torque measurements. The solid line is the $1/\cos \Theta$ fit with $F_0 = 4890$ T for $\Theta = 0$. This means that the cylindrical Fermi surface fills about half of the first Brillouin zone in agreement with the stated band filling of 0.75 and a charge transfer of 2:1. The value for F_0 is about 2.2% smaller than reported by Mori *et al.* [6]. Our data have a much higher signal-to-noise ratio with neither strange node-like features in the SdH signal (see Fig. 3 in [6]) nor an unusal saw-tooth shape of the torque signal (Fig. 4 in [6]). Therefore, our data allow a much more reliable extraction of the band-structure parameters of (BEDO-TTF)$_2$Cl$_2$(H$_5$O$_2$).

The LK theory for 3D metals predicts a temperature dependent damping of the oscillation amplitude which is given by $A_r \propto T / \sinh(\alpha r \mu_c T / B)$, where $\alpha =$
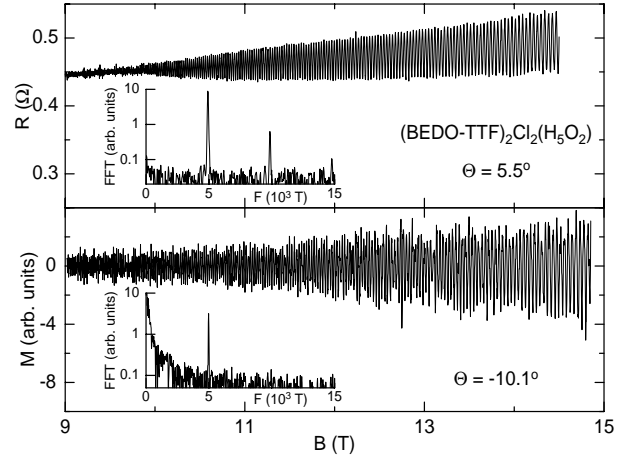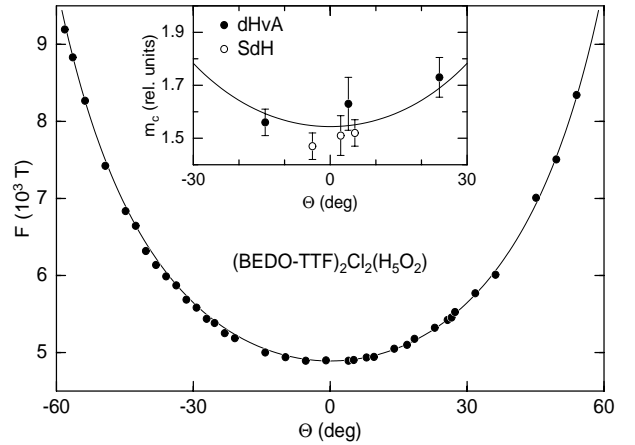

Fig. 4. Angular dependences of the dHvA frequency and the effective cyclotron mass (inset). The solid lines are $1/\cos \Theta$ fits with values for $\Theta = 0$ of $F_0 = 4890$ T and $m_c = 1.54 m_e$, respectively.

$2\pi^2 k_B m_e / e\hbar = 14.69$ T/K and r is the number of the harmonic. We determined the effective cyclotron mass $\mu_c = m_c / m_e$ from the temperature dependence of the dHvA and SdH oscillation amplitudes for six different angles. The result is shown in the inset of Figure 4. Caused by a strong damping of the oscillation amplitudes at higher angles the effective cyclotron mass could only be determined up to 24°. The m_c data from SdH measurements (open circles) are somewhat smaller than extracted from the dHvA experiment (closed circles). However, the overall angular dependence follows within error bars the expected 2D behavior $m_c = m_{c0} / \cos \Theta$ with $m_{c0} = (1.54 \pm 0.05) m_e$ (solid line). We checked for a possible field dependence of m_c which is indicative for strongly 2D materials and has been observed for some organic conductors [12,13]. Within
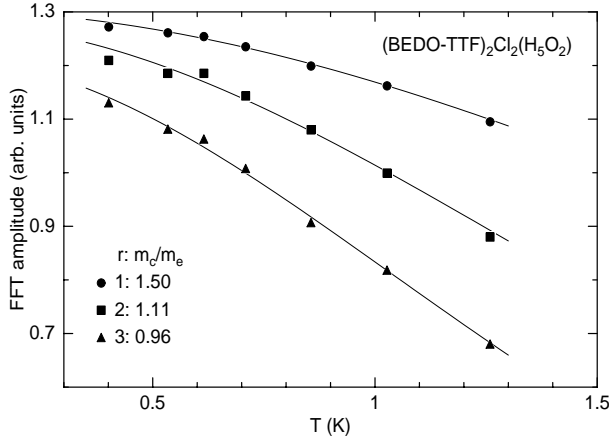
Fig. 5. Temperature dependence of the dHvA oscillation amplitude for the fundamental ($r = 1$), the second harmonic ($r = 2$, scaled by a factor of 23.5), and the third harmonic ($r = 3$, scaled by a factor of 50) extracted from Fourier transformation of data between 26 and 28 T at $\Theta = -14.2°$. The solid lines are fits according to the Lifshitz–Kosevich theory as explained in the text.

Fig. 6. Amplitude of the fundamental frequency of the torque dHvA signal at $T = 0.4$ K for sweeps 20 T $\leq B \leq$ 23 T vs. $1/\cos\Theta$ for two samples of $(BEDO\text{-}TTF)_2Cl_2(H_5O_2)$. The strong reduction of the amplitude of sample A at $1/\cos\Theta = 1.1$ is probably due to twinning.

error bars we could not find a definitive reduction of m_c with field. However, we observed a discrepancy of m_c extracted from different harmonics *via* the LK theory. The higher the harmonics the smaller effective masses were deduced. As an example Figure 5 shows the temperature dependence of the fundamental ($r = 1$), second ($r = 2$), and third ($r = 3$) harmonic of the dHvA oscillation amplitudes at $\Theta = -14.2°$ obtained from Fourier transformations between 26 and 28 T. The solid lines are fits according to the LK theory with m_c's as given in the figure. The apparent reduction of m_c for higher harmonics is known to occur when magnetic-interaction-like feed back is present [14] which may be caused either by a large susceptibility of the electron gas or by torque interaction. However, these effects can be excluded because of the very weak magnetization of the sample and the small torquemeter amplitude in the present case. It is much more probable that the deviation from simple LK theory is a manifestation of the 2D nature of the electronic band structure. For an ideal 2D system the chemical potential μ is no longer independent of field but oscillates with the Landau levels crossing the Fermi energy. This in turn leads to a saw-tooth shape of the dHvA oscillations *vs.* field with a strongly enhanced harmonic content. This was shown by numerical [15] and analytic [16] calculations. However, neither the numerical simulation nor the analytic theory can be applied as easily to measured data as the LK theory. In [15] it was stated explicitly that the higher harmonics of the dHvA oscillations in a 2D electron gas are apparently reduced when extracted with the LK theory. The amount of this reduction as well as the harmonic content sensitively depends on the scattering rate, *i.e.*, the Dingle temperature T_D of the sample. The large T_D present in our sample (see below) leads to broadened Landau levels with a much more continuous density of states and a less oscillating chemical
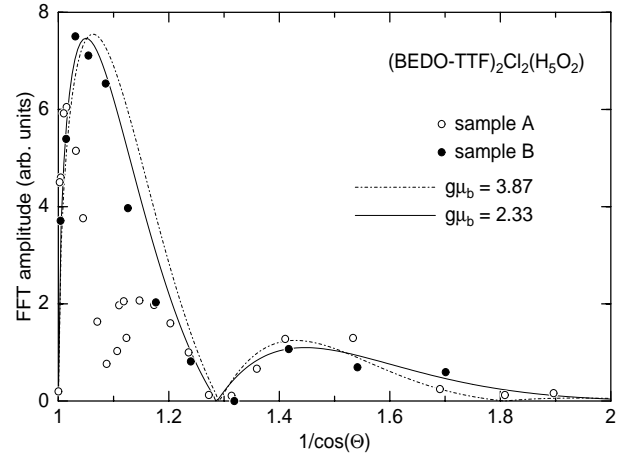
potential. Therefore, the predicted deviations from conventional 3D LK theory are much less pronounced than expected from simply comparing the bandwith perpendicular to the ET planes (see below) with $\hbar\omega_c$ which is about 2.1 meV at 28 T.

The oscillating chemical potential has a similar effect on the dHvA line shapes as a large oscillating susceptibility, dM/dB, which leads to magnetic interactions [16,17]. We, therefore, applied to our data the concept of magnetic interactions [14] which gives an approximative description of the temperature dependence of the dHvA amplitude for an electron gas with large susceptibility dM/dB. For weak higher harmonics one obtains $A_r \propto A_1^r \propto [T/\sinh(\alpha\mu_c T/B)]^r$ [14]. Analysis of the data shown in Figure 5 yields $m_c(r = 2) = 1.55 m_e$ and $m_c(r = 3) = 1.60 m_e$ which agrees very well with the value for $r = 1$.

The determination of T_D is somewhat hampered by the twinning of sample A and D (see below). However, as will be shown later, T_D presumably is larger than 5 K. Therefore, conventional 3D LK theory would predict negligible harmonics in the magnetic quantum oscillations [14]. However, we find a strong harmonic content both in the SdH and dHvA data. The very good realization of an almost perfect 2D electronic structure is also evident from the absence of nodes in the dHvA signals of sample B and C. This proves that the indications of nodes in the other two samples are most probably due to twinning. It further gives an upper estimate of the transfer integral t between the BEDO-TTF layers which is a measure of the electronic three dimensionality. t must be smaller than $\epsilon_F/2000 \approx 0.18$ meV, where ϵ_F is the Fermi energy and we have assumed a circular Fermi surface [18,19]. In view of our results the nodes observed in [6] presumably are due to twinning of the sample.

The angular dependence of the dHvA oscillation amplitudes of the samples A and B is shown in Figure 6. The exact form of this dependence is given by the band structure parameters m_c, T_D, and $g\mu_b$. In especially, the angles where the fundamental amplitude vanishes is determined by the spin-splitting parameter $g\mu_b(\Theta) = 0$, where $g = g_{ESR}/(1+\lambda'_{ee})$ is the conduction electron g factor determined by ESR renormalized by electron-electron interaction λ'_{ee} and $\mu_b = \mu_c/(1 + \lambda)$ is the effective cyclotron mass without electron-phonon interaction λ [14]. The strong reduction of the dHvA amplitude at higher angles is direct evidence for a large Dingle temperature. The lines in Figure 6 are fits of the torque dHvA amplitude according to the LK formula [14]. The parameters were $\mu_{c0} = 1.54/\cos\Theta$, $T_D = 5.8$ K, and $g\mu_{b0} = 2.33$ (3.87) for the solid (dashed) line. We find a strong deviation of the fit from the experimental data of sample A at lower angles around $1/\cos\Theta \approx 1.1$. This is a manifestation of the twinning of this sample. At this angular range and within the field window (20 T $\leq B \leq 23$ T) where data were taken a node occurred. This is proven by the fact that the dHvA amplitude of sample B does not show this deviation but can be well-described by the fit line over the whole angular range. The high Dingle temperatures of both samples prevent a definite determination of a second spin-splitting zero. This is the reason for the two possible $g\mu_{b0}$ values (either 2.33 or 3.87). For $g\mu_{b0} = 3.87$, g must be larger than $g\mu_b/\mu_c = 2.5$, exactly this value for $\lambda = 0$. This would mean that an appreciable electron-electron interaction (as found for other organic superconductors [19]) is relevant for the present material. The other possibility, $g\mu_{b0} = 2.33$, hints to an appreciable electron-phonon coupling which would be $\lambda = m_c/m_b - 1 = 0.32$ for a negligible electron renormalization λ'_{ee}, *i.e.*, $g = g_{ESR} = 2$. Usually, λ'_{ee} is small and negative [14] which in turn would lead to a larger g and, therefore, even larger λ. For a decisive discussion of this puzzle additional work on a better quality crystal or in higher fields would be helpful. This would allow a precise determination of $g\mu_{b0}$.

4 Conclusion

SdH and dHvA results show consistently that the Fermi surface of the organic metal bis(ethylenedioxy)-tetrathiafulvalene chloride corresponds to half the Brillouin zone. This proves a charge transfer of one electron per two BEDO-TTF molecules. Together with structural X-ray data the only possible stoichiometry is therefore (BEDO-TTF)$_2$Cl$_2$(H$_5$O$_2$). Compared to other organic metals a rather low effective cyclotron mass of $m_c = (1.54 \pm 0.05)m_e$ was found. The observed spin-splitting zero hints to either appreciable electron-electron or electron-phonon interactions. The absence of any nodes caused by a corrugated Fermi cylinder and discrepancies to the Lifshitz–Kosevich theory for higher harmonics indicate a highly two-dimensional character of the electronic system. By applying for the oscillatory chemical potential the concept of magnetic interactions allows for the temperature dependence of the magnetic quantum oscillations a consistent determination of m_c also from higher harmonics.

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