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Unusual magnetic quantum oscillations in organic metals at high magnetic fields

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Abstract

We report on Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) results for the highly two-dimensional (2D) organic superconductors κ-$(ET)_2I_3$ (T_c = 3.5 K) and β''-$(ET)_2SF_5CH_2CF_2SO_3$ (T_c = 4.4 K). The SdH oscillations of both materials show an apparent deviation from the well-understood 2D dHvA signal at low temperatures and high magnetic fields. For κ-$(ET)_2I_3$, the mechanism leading to this behavior still needs to be clarified. For β''-$(ET)_2SF_5CH_2CF_2SO_3$, an anomalous steady background part of the magnetoresistance seems to account for the observed discrepancies.

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1. Introduction

The organic metals and superconductors of the type $(ET)_2X$, where X represents a monovalent anion and ET (= BEDT-TTF) is the organic donor molecule bisethylenedithio-tetrathiafulvalene, are characterized by their quasi-two-dimensional (2D) electronic structure [1]. These charge-transfer salts are available as high-quality crystals enabling the detection of well-developed de Haas–van Alphen (dHvA) and Shubnikov–de Haas (SdH) oscillations [2]. Thereby, the dHvA signals are well understood either by the conventional 3D Lifshitz–Kosevich (LK) theory [3] or by 2D theoretical models [4,5]. Pronounced 2D dHvA oscillations are realized at

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sufficiently high fields for the organic superconductors κ-$(ET)_2I_3$ (T_c = 3.5 K) [6] and β''-$(ET)_2SF_5CH_2CF_2SO_3$ (T_c = 4.4 K) [7]. Although the dHvA signals are in line with the 2D models, the oscillations in the transport data behave highly unusual for these materials [8–11]. The origin for these unexpected apparent discrepancies between resistance and thermodynamic quantum oscillations is largely unknown. Here, we report on new SdH measurements extending the field-temperature ratio to B/T = 33 T/50 mK for κ-$(ET)_2I_3$ and to B/T = 60 T/0.6 K for β''-$(ET)_2SF_5CH_2CF_2SO_3$.

2. Experimental

The investigated single crystals were grown by standard electrocrystallization techniques [12,13]. For the transport measurements thin gold wires used as current leads were glued with graphite paste to the samples. The interplane resistance was measured by use of either a lock-in amplifier or a four-point low-frequency ac-resistance bridge feeding a current of a few μA through the samples. The magnetic field was oriented perpendicular to the BEDT-TTF planes, i.e., *parallel* to the current. The crystals were investigated at the National High Magnetic Field Laboratory at Tallahassee in fields up to 33 T and at Los Alamos in pulsed fields up to 60 T. The very low temperatures down to 35 mK were provided by a dilution refrigerator. Otherwise, ^{3}He cryostats were used. The dHvA signals were detected by use of cantilever torque magnetometers (see Refs. [6,7]).

3. Results and Discussion

3.1. κ-$(ET)_2I_3$

The magnetoresistance data of κ-$(ET)_2I_3$ [Fig. 1(a)] clearly reveal pronounced SdH oscillations with frequencies of about 575 T and 3900 T. These SdH frequencies correspond to the so-called α pocket and the magnetic-breakdown β orbit of the calculated Fermi surface, respectively [14]. A comparison with the dHvA signal [Fig. 1(b)] shows that the slow α-orbit oscillation appears much more enhanced in the SdH signal. Furthermore, the oscillating torque signal grows considerably stronger with field than the resistive oscillations in the transport data. This becomes much clearer in the Dingle plot shown in Fig. 1(c) where the oscillation amplitudes A_i extracted from Fourier transformations over short field ranges (Fig. 2) are multiplied by $\sinh(X_i)$ and plotted as a function of $1/B$. Thereby, $X_i = (2\pi^2 k_B/e\hbar)\, m_c T/B$, with m_c the effective cyclotron mass. In this plot, only the dHvA data [open circles in Fig. 1(c)] follow a straight line as predicted by models for 2D electronic systems [3,5]. The SdH data for the α orbit (closed squares) saturate towards higher fields (smaller $1/B$). This is, at least partially, caused by magnetic breakdown which reduces the probability for the charge carriers to traverse the α orbit at high fields. Correspondingly, the oscillation amplitude for the β orbit should increase. On the contrary, the SdH amplitude for this orbit (closed circles) even decreases at the highest fields.

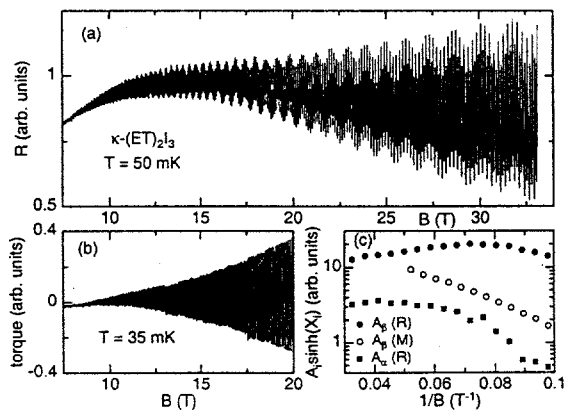

Fig. 1. Field dependences of (a) the interlayer resistance of κ-$(ET)_2I_3$ at T = 50 mK and (b) the torque signal at 35 mK. (c) Dingle plot for the amplitudes of the fundamental SdH and dHvA oscillations.

Besides this unusual field dependence an equally unexpected temperature dependence of the SdH amplitudes is found (inset of Fig. 2). At low fields (10 T) the SdH amplitudes increase with decreasing temperature in line with theory and dHvA data [6,15]. LK fits (solid lines in the inset of Fig. 2) yield effective masses of 2.1(4) m_e for the α orbit and 3.6(3) m_e for the β orbit. At high fields (29 T), the SdH amplitude of the β oscillation decreases towards lower temperatures in sharp contrast to theoretical predictions. This behavior, previously reported for SdH data at higher temperatures [8,9], might be connected with localization effects of the 2D electrons [9]. A final answer to this problem is, however, far from being found.

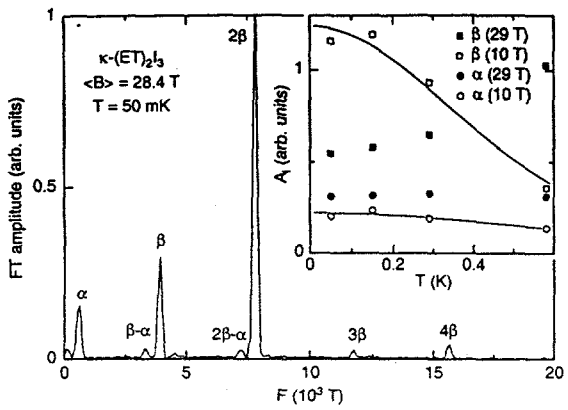

Fig. 2. The Fourier spectrum of the data shown in Fig. 1 between 25 and 33 T. The inset shows the temperature dependences of the fundamental SdH amplitudes for two different fields. The solid LK fit lines result in effective masses in line with dHvA values.

3.2. β''-$(ET)_2SF_5CH_2CF_2SO_3$

High-field dHvA investigations have revealed that β''-$(ET)_2SF_5CH_2CF_2SO_3$ has an ideal 2D Fermi surface [6]. The dHvA oscillations show an inversed saw-tooth behavior and can quantitatively be described by a 2D theory with fixed chemical potential which requires the existence of a large density of states at the Fermi level. This, therefore, indicates the existence of the predicted [16] – but never directly observed – 1D bands. At sufficiently high magnetic fields one therefore could expect to detect a new quantum oscillation frequency caused by magnetic breakdown. However, up to 60 T neither dHvA [10] nor transport data (Fig. 3) show any indication for an additional frequency besides the well-known ~200 T oscillation. This hints to a larger energy gap between the two bands at the Fermi level as predicted by band-structure calculations [16].

Contrary to the dHvA signal, the transport data seem to result in a SdH signal not in line with the dHvA results (see the inset of Fig. 3 and Refs. [10,11]). Thereby, the SdH signal is given by the relative conductance oscillations $\Delta\sigma/\sigma = \sigma/\sigma_b - 1$, where σ_b is the steady background part of the conductance σ. In the present case where the Hall component of the resistivity tensor is negligible, the SdH signal can be written as $\Delta\sigma/\sigma = R_b/R - 1$. With the background resistance R_b estimated by a polynomial fit to the measured resistance R, the SdH signal shown in the inset of Fig. 3 results. While at lower fields the signal is in line with the conventional behavior and dHvA results, the oscillation amplitude decreases with decreasing temperature at higher fields.

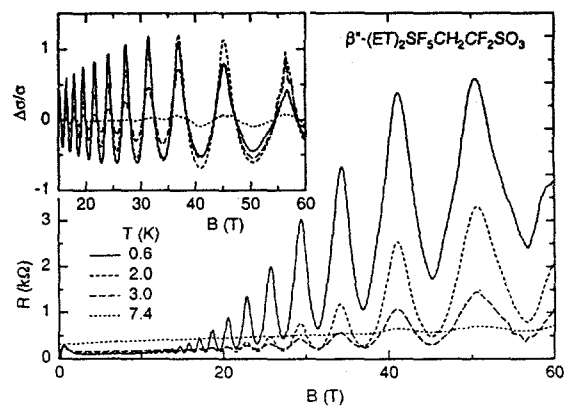

Fig. 3. The field-dependent resistance of β''-$(ET)_2SF_5CH_2CF_2SO_3$ for different temperatures measured by a dc technique in pulsed fields up to 60 T. The inset shows the SdH signal obtained by using a polynomial fit for the background magnetoresistance.

On first sight, this is reminiscent of the behavior found for κ-$(ET)_2I_3$ [9] as discussed above. For β''-$(ET)_2SF_5CH_2CF_2SO_3$, however, a very strong field and temperature dependence of R_b is evident. Indeed, at high fields and low temperatures an insulating behavior is found [11], i.e., the resistance increases with decreasing temperature. For κ-$(ET)_2I_3$ the resistivity remains metallic even up to the highest fields. This leads to the question on how R_b might correctly be determined. For a multi-band metal as in the present case the SdH signal originating from one band is connected to the partial density of states for that band. Therefore, the conductivity caused by charge carriers of this band has to be disentangled from the measured resistance. This is *a priori* not possible since the field and temperature dependence of the conductivity of the 1D-band charge carriers cannot be measured independently. Nevertheless, a more reliable estimate of R_b is possible by a direct comparison of the dHvA and SdH signals for one sample. Theory predicts that the SdH signal, $\Delta\sigma/\sigma$, is proportional to the derivative of the oscillating magnetization times B^2 [3]. In the upper part of Fig. 4 the latter signal is shown in comparison with the SdH signal which is extracted from the measured resistance of the same sample by use of the shown R_b. A reasonable agreement between both oscillating signals is achieved. Thereby, R_b lies at the upper

limit of the oscillating signal in R. For smaller R_b, i.e., choosing the oscillation average for R_b, the temperature and field dependence of $\Delta\sigma/\sigma$ would be similar as shown in the inset of Fig. 3 and, therefore, contradict the dHvA results.

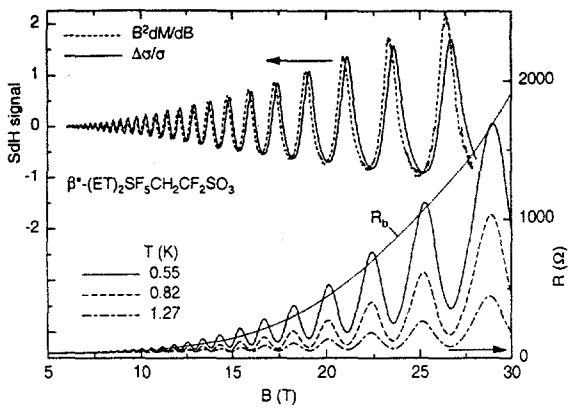

Fig. 4. The resistance of another β''-$(ET)_2SF_5CH_2CF_2SO_3$ sample for different temperatures measured in static fields up to 30 T. The SdH signal $\Delta\sigma/\sigma$ (solid line in the upper part of the figure) resulting from the shown background resistance R_b in comparison to the derivative of the dHvA signal times B^2 of the same sample.

Although the chosen R_b seems to be somewhat arbitrary, the good agreement with the dHvA data renders the choice reasonable. This means that an additional transport channel must contribute to the conductivity which presumably is caused by charge carries from the 1D bands. In previous high-field SdH investigations for other organic metals comparable apparent deviations from the LK theory were reported [17,18]. It seems to be plausible that those are caused by a similar ambiguities in choosing R_b. It remains, however, questionable whether the same is true for the observed behavior of the SdH signal of κ-$(ET)_2I_3$. For this material at high magnetic fields, i.e., deep in the magnetic-breakdown regime, all charge carriers should contribute to the oscillating signal leaving no room for an additional conductivity channel.

4. Conclusions

For the highly 2D organic metals κ-$(ET)_2I_3$ and β''-$(ET)_2SF_5CH_2CF_2SO_3$ the magnetic quantum oscillations in strong magnetic fields deviate from the conventional 3D theory. While the modified dHvA oscillations can be described by appropriate 2D scenarios [6,7], the SdH signals show an apparent deviation from the theoretical behavior. For β''-$(ET)_2SF_5CH_2CF_2SO_3$, a reasonable choice of the strongly field and temperature-dependent background resistance leads to a SdH signal which agrees well with the expected behavior. The transport data of κ-$(ET)_2I_3$ do not suggest a comparable strong temperature and field dependence of R_b necessary to account for the observed unusual SdH signal. An additional mechanism like localization effects might be the cause for the saturating SdH amplitude at low temperatures and high fields.

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