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(Invited talk)

DE HAAS - VAN ALPHEN STUDIES AND FERMI SURFACE PROPERTIES OF ORGANIC SUPERCONDUCTORS $(ET)_2X$

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ABSTRACT

de Haas - van Alphen (dHvA) measurements of organic superconductors $(ET)_2X$, where ET stands for bis(ethylene)dithiotetrathiafulvalene (or BEDT-TTF) and X = IBr_2, $(NH_4)Hg(SCN)_4$ and $Cu(NCS)_2$ are reported. The strong two-dimensionality of the Fermi surface (FS) is clearly seen by the perfect $1/\cos(\Theta)$-behavior of the dHvA frequency. The distinctive kind of beating and the angular dependence of the dHvA signal in β-$(ET)_2IBr_2$ gives clear evidence for a lightly corrugated structure of the FS. Due to the nearly cylinder-shape of the FS the bare band structure effective mass, m_b, also shows a $1/\cos(\Theta)$-dependence which is responsible for spin splitting zeros at certain angles. At these points, where the fundamental amplitude of the dHvA signal is vanishing, m_b could exactly be determined and by comparison with the independently measured cyclotron effective mass the electron-phonon coupling constant could be estimated.

INTRODUCTION

The largest number of organic superconductors with T_c's up to 13 K, charge transfer salts of the type $(ET)_2X$, are characterised by their nearly two-dimensional (2D) electronic properties [1]. With the availability of very good single crystals during the last years the 2D electronic band structure and, in particular, the Fermi surface (FS) was investigated by numerous Shubnikov-de Haas (SdH) and de Haas-van Alphen (dHvA) experiments [2].

In this paper, we present results of our detailed dHvA-study of the angular dependence of the extremal area of the FS, the cyclotron effective mass and the dHvA amplitude of β-$(ET)_2IBr_2$, α-$(ET)_2(NH_4)Hg(SCN)_4$ and κ-$(ET)_2Cu(NCS)_2$. Previous measurements of the SdH effect in the former show contrary results concerning the FS structure [3, 4]. With our dHvA measurements we were able to investigate this discrepancy with a different method. We found beating of the dHvA signal over a wide angular range of the applied magnetic field reflecting the corrugated structure of the FS in this compound. In all investigated crystals we found a $1/\cos(\Theta)$-dependence of the extremal areas of the FS and consequently of the effective masses resulting in an unusual angular dependence of the dHvA amplitude and leading to directly observable spin-splitting far from the quantum limit.

EXPERIMENTAL

The high-quality crystals were grown by the usual electrocrystallization as described in detail elsewhere [5]. The irregular-shaped platelike samples with an area of ~0.8x0.8 mm^2 and a thickness between 0.1 and 0.5 mm were mounted in a rotatable sample holder and oriented with a four-circle x-ray diffractometer. The dHvA effect was measured by a field modulation technique in a ^3He cryostat in fields up to H = 15 T and temperatures down to 0.45 K. The cyclotron effective masses $\mu_c = m_c/m_e$ were obtained by the conventional method [6], i. e. by measuring the temperature dependence of the dHvA amplitude, M(T), and fitting the data to $M(T)/T \propto \sinh^{-1}(\alpha\mu_c T/H)$ with $\alpha = 2\pi^2 k_B m_e/e\hbar = 14.69$ T/K.

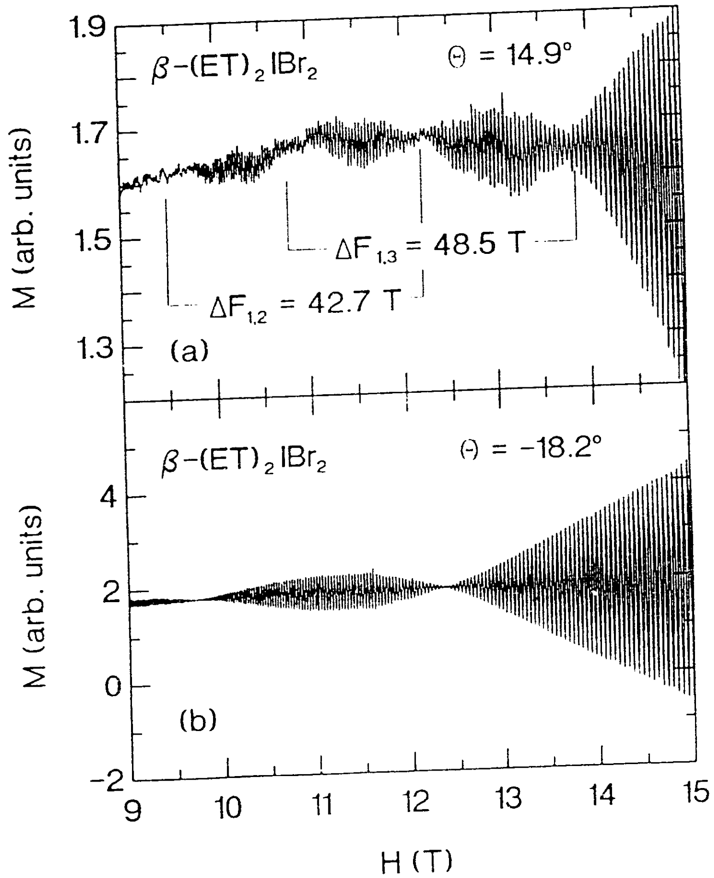

Fig.1. Magnetization of β-$(ET)_2IBr_2$ vs. magnetic field, applied at angles Θ = 14.9° (a) and Θ = -18.2° (b) normal to the conducting planes.

RESULTS AND DISCUSSION

The six measured samples of β-$(ET)_2IBr_2$ all show the same principal behavior of the dHvA signals but with different amplitudes of the oscillations due to different sample quality and volume of the crystals. In the following we focus mainly on the crystal showing the largest dHvA amplitude with the lowest Dingle temperature $T_D \approx 1.1$ K. The magnetization of this sample was measured for more than 70 different field orientations Θ, where Θ denotes the angle between field and the normal to the highly conducting (a,b)-plane.

In all investigated samples and at almost all angles where dHvA oscillations were visible we found nodes in the dHvA signal. Fig. 1 shows examples of this beating behavior for two angles. For Θ = 14.9° between 9 and 15 T four nodes of the dHvA signal are found (Fig. 1a), two with nearly zero remaining amplitude at ~9.5 T and ~12.2 T, and two nodes with finite amplitude at ~10.8 T and ~13.9 T. This unusual behavior can only be explained with the existence of four slightly different frequencies, F_1 to F_4, with an average frequency F_{av} = 3976±20 T and the differences $\Delta F_{1,2}$ (= F_2 - F_1) = $\Delta F_{3,4}$ = 42.7±0.3 T and $\Delta F_{1,3}$ = $\Delta F_{2,4}$ = 48.5±0.3 T. The amplitudes of the beats require that the pair F_3, F_4 has the same amplitude, ~25% higher than that of pair F_1, F_2. A different dHvA amplitude for different cyclotron orbits is quite normal and can be easily understood. Assuming the usual proportionality between the cyclotron band-structure mass and the derivative of the cyclotron orbit with respect to energy, $m_b \propto \partial A/\partial E$, the area differences, $\Delta A = (2\pi e/\hbar)\Delta F$, of the order 1.2% will also be reflected in different masses. From our measurements we obtain for the cyclotron resonance mass at this angle $m_c \approx 4.2 m_e$ (see Fig. 4) and a Dingle temperature $T_D \approx 1.1$ K. The overall angular dependence of the absolute amplitude gives some hints for a band-structure mass of ~$3.6 m_e$ [7]. Taking these values with 1.2% difference in m_b and m_c for the two pairs of frequencies the dHvA signal shown in Fig. 1a can be very well described as will be discussed elsewhere.

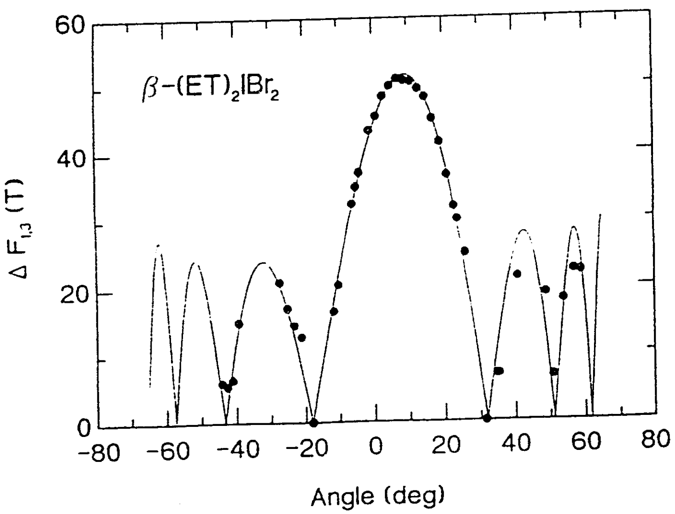

Fig. 2. Angular dependence of the beating frequency $\Delta F_{1,3}$ in β-$(ET)_2IBr_2$ with fit curve (2).

By a systematic investigation of the angular dependence of the frequency differences we found for $\Delta F_{1,2}$ (= $\Delta F_{3,4}$) a symmetric increase which can be approximated by $\Delta F_{1,2}$ = 24.6 T + 17.75 T/cos(Θ). This is in sharp contrast to the angular change of $\Delta F_{1,3}$ (= $\Delta F_{2,4}$) showing the asymmetric nonmonotonic behavior plotted in Fig. 2. At certain angles where $\Delta F_{1,3}$ = 0 only two different frequencies remain and at these angles the amplitude of the dHvA oscillations becomes extremely large. As an example, Fig. 1b shows the measured dHvA signal close to one of these points at Θ = -18.2° with $\Delta F_{1,2}$ = 43.2 T, where the amplitude is larger by a factor of 10 compared to Fig. 1a (note the different scale of the ordinate).

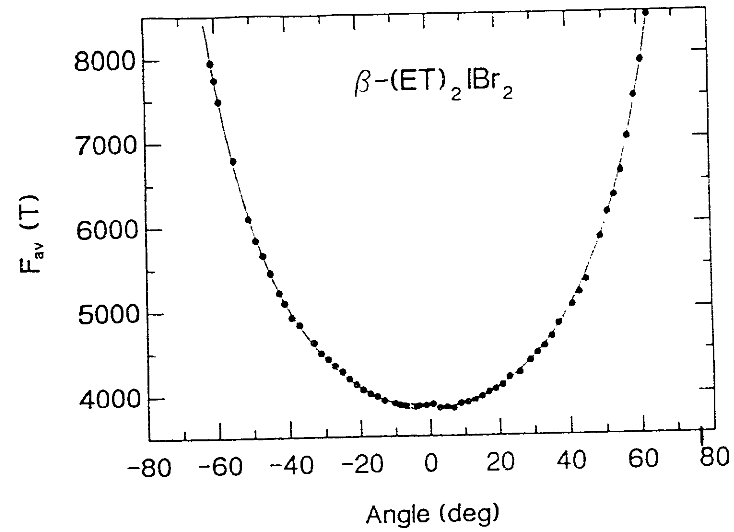

Fig. 3. Angular dependence of the average frequency in β-$(ET)_2IBr_2$. The solid line shows the 1/cos(Θ)-behavior.

The average frequency, F_{av}, on the other hand, shows the angular dependence $F_{av} = F_o/\cos(\Theta)$ expected for a cylindrical FS with the fit parameter F_o = 3842±10T. Fig. 3 shows the data points and the solid fit line. The obtained area of the FS of $3.67 \cdot 10^{15}$ cm^{-2} is consistent with band structure calculations [8] and with SdH measurements of a Russian group [4], but in sharp contrast to the SdH results of Ref. 3, where an unsystematic angular change of the SdH frequency and a FS area of approximately half the value stated here was reported.

The distinctive angular behavior of $\Delta F_{1,3}$ and the dHvA amplitude can be understood by a simple model for a k_z-modulation supporting one minimal and one maximal orbit [9]. Taking an asymmetric energy dispersion curve [10]

$$\varepsilon_k = \frac{\hbar^2}{2m_b}(k_x^2 + k_y^2) - 2t\cos(c'k_z + u_x k_x + u_y k_y), \qquad (1)$$

with t being the interlayer transfer energy for hopping along a vector **h** = (u_x, u_y, c') and neglecting for the moment the present in-plane anisotropy [8, 10], the angular dependence of the frequency difference of the extremal areas is obtained as

$$\Delta F \cos(\Theta) = \Delta F_{o\varphi} J_o(c' k_F \tan(\Theta) - \mathbf{u}_\parallel \mathbf{k}_\parallel). \quad (2)$$

$J_o(x)$ is the Bessel function of zeroth order, $\mathbf{u}_\parallel = (u_x, u_y, 0)$ is the in-plane component of the hopping vector, $\mathbf{k}_\parallel$ is the Fermi wave-vector resulting from the cut of the x,y-plane with the field rotation plane and $\Delta F_{o\varphi}$ is a parameter depending on t and the angle φ between the field rotation plane and $\mathbf{u}_\parallel$. Calculating c′ = 1.495 nm from the room temperature lattice parameters, k_F from $F_{av} = \hbar k_F^2/2e$ and taking the parameters $\Delta F_{o\varphi}$ = 51 T and $|\mathbf{u}_\parallel|$ = 0.1 we obtain the very good description of $\Delta F_{1,3}(\Theta)$ shown by the solid line in Fig. 2. For the case shown in Fig. 2 with H ⊥ b the maximum asymmetry was observed corresponding to a field rotation in the $(\mathbf{u}_\parallel, z)$-plane. This means that $\mathbf{u}_\parallel$ is pointing perpendicular to the b-axis and the angle between **h** and **c*** is $\arctan(u_\parallel/c') \approx 8°$. This is in very good agreement with a determination of **h** from measurements of the angular magnetoresistance oscillations [10] and can be understood by the triclinic structure of the salt discussed here where c is tilted by 7.4° with respect to c* [11]. The interlayer transfer integral can be obtained from $\Delta F_{o\varphi} = 4m_b t/\hbar e$ for this rotation plane and is $t/\varepsilon_F \approx 1/300$. A symmetric angular change of $\Delta F_{1,3}$ was observed for rotation of the field in the (b,z)-plane [7].

The extraordinary large amplitudes of the dHvA signal, seen for example in Fig. 1b, coincide nicely with the zero points of the Bessel function and can also be explained by the energy dispersion (1). At these angles the cross-sectional area of the FS is constant over the whole Brillouin zone and the curvature factor $(\partial A/\partial k_H)^{-1/2}$, also relevant for the dHvA amplitude [6], becomes maximal.

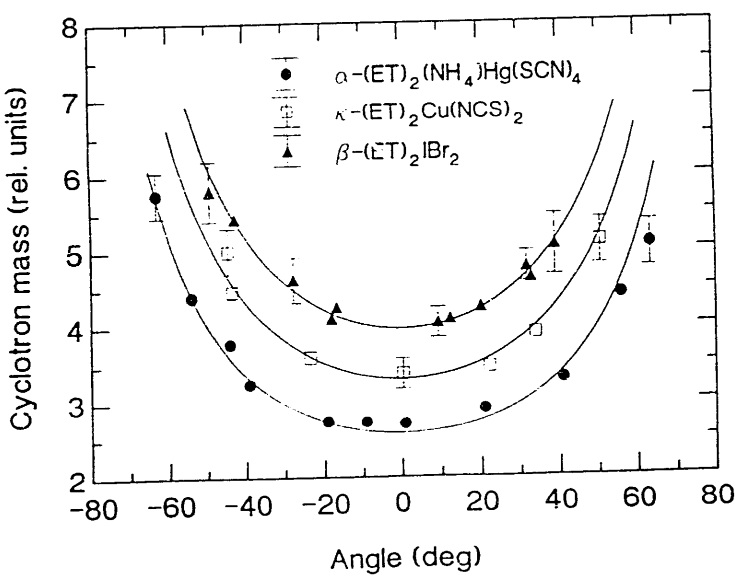

Fig. 4. Cyclotron effective mass of the three investigated organic superconductors versus angle of the applied magnetic field. The solid lines are 1/cos(Θ)-fits as described in the text.

The reason for the appearance of the additional frequencies F_2 and F_4 is unknown at the moment. One possible explanation would be the assumption of four highly asymmetric bulges on the FS [12]. On the other hand, the identical effective masses and the special angular dependence of $\Delta F_{1,2}$ suggests magnetic interaction as a possible mechanism for the observed behavior.

We now want to focus on the angular dependence of the effective masses. Fig. 4 shows the measured cyclotron effective masses m_c vs. Θ for three different (ET)-salts. Common for all compounds is an increasing m_c with angle Θ. A behavior which can be quite reasonably fitted by $m_c = m_{co}/\cos(\Theta)$ with values m_{co} of $(2.6\pm0.1)m_e$, $(3.3\pm0.2)m_e$ and $(4.0\pm0.1)m_e$ for X = $(NH_4)Hg(SCN)_4$, X = $Cu(NCS)_2$ and X = IBr_2, respectively. As discussed earlier in detail in separate publications [13, 14] a different fit of $m_c(\Theta)$ with an additional constant term is also possible and gives a slightly better description of the measured data. The increasing effective mass is easily understandable by the two-dimensionality of the FS resulting in an increasing cross-sectional area A and, therefore, the growing m_b proportional to $\partial A/\partial E$.

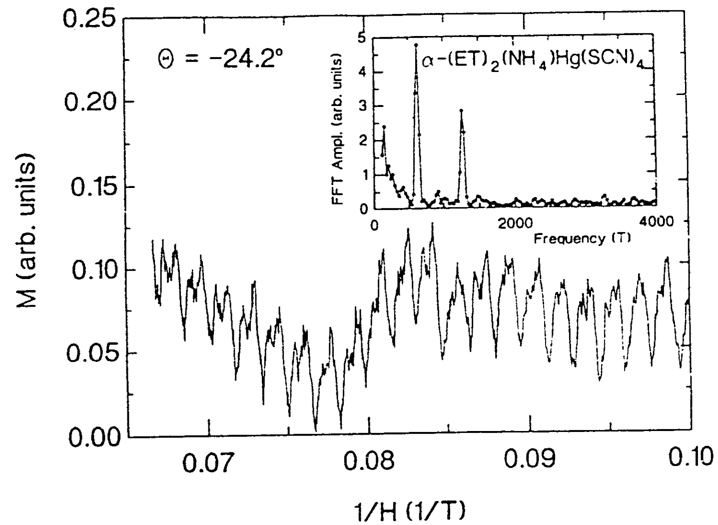

Fig. 5. Magnetization of α-$(ET)_2(NH_4)Hg(SCN)_4$ vs. the reciprocal field at Θ = -24.2°. The inset shows the Fourier transformation of the data.

The 1/cos(Θ)-behavior of m_b has drastic effects on the angular dependence of the dHvA amplitude. At certain angles where $m_b = (n-0.5)\cdot m_c$ with n = 1,2,3... the spin-splitting factor $\cos(r\pi g m_b/2m_e)$, in the Lifshitz-Kosevich expression becomes zero for the fundamental frequency (r = 1) and 1 for the second harmonic (r = 2). Therefore, from the harmonic ratio, i. e. the amplitude of the fundamental, M_1, divided by the second harmonic, M_2, and with the by ESR measurements well-known g-values of g ≈ 2 [15, 16], the band-structure mass m_b for X = $(NH_4)Hg(SCN)_4$ and X = $Cu(NCS)_2$ could be determined [13, 14]. An example where M_1 is almost zero, a so-called spin-splitting zero (SSZ), is shown in Fig. 5 for α-$(ET)_2(NH_4)Hg(SCN)_4$. In this compound the first SSZ's are around ±26°, where $m_b = 2.5m_e$, so that a reasonable dHvA signal is still observable. In Fig. 5 the measured magnetization is plotted vs. the inverse field. Especially, for high fields a clear splitting of the oscillations is visible. The Fourier transformation, plotted in the inset of Fig. 5, shows this more quantitatively. The first peak at ~630 T representing the amplitude of the fundamental is only a factor of ~1.5 larger than the peak at ~1260 T belonging to the second harmonic. At higher angles and in the other compounds where the effective mass is larger the spin splitting was not so clearly observable because the amplitude of the second harmonic hardly exceeded the noise level. However, from the angles where the fundamental vanishes a perfect $1/\cos(\Theta)$-behavior of m_b could be deduced. By comparison of m_b and the by electron-phonon interaction enhanced cyclotron mass shown in Fig. 4 the coupling parameter λ could be determined from $m_c = m_b(1+\lambda)$. With the simplest form of the BCS formula $T_c \approx 1.14 \cdot \Theta_D \cdot \exp(-1/\lambda)$ estimations of superconducting transition temperatures yield values in a reasonable range of ~0.6 K for X = $(NH_4)Hg(SCN)_4$ and ~ 6 K for X = $Cu(NCS)_2$ consistent with the actually observed values of T_c. In β-$(ET)_2IBr_2$ the determination of the angular dependence of m_b was severely hampered by the mentioned extremal changes of the dHvA amplitude due to the warped FS structure. Nevertheless, close to $\Theta = 0°$ always very small amplitudes were measured which can be ascribed to a spin-splitting zero with $m_b \approx 3.5$, the largest possible effective mass for $g \approx 2$. With this value a T_c of approximately 0.65 K is obtained still in order of magnitude agreement with the experimental $T_c \approx 2.5$ K.

CONCLUSIONS

In all investigated (ET)-compounds the characteristic 2D $1/\cos(\Theta)$-behavior of the extremal area of the FS consistent with band-structure calculations was found. A small warping of the FS in β-$(ET)_2IBr_2$ was observed by destinctive angular dependent beating phenomena. The $1/\cos(\Theta)$ change of the effective mass explains the angular dependence of the dHvA amplitude and the appearence of spin-splitting zeros at certain angles. With our data the electron-phonon coupling constant could be estimated resulting in T_c's which are in qualitative agreement with the actually observed critical temperatures.

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