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de Haas–van Alphen studies of the organic superconductors α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ and κ-(ET)$_2$Cu(NCS)$_2$ [with ET = bis(ethelenedithio)-tetrathiafulvalene]

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We report measurements of the de Haas–van Alphen (dHvA) effect in the organic superconductors α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ and κ-(ET)$_2$Cu(NCS)$_2$ in fields up to 15 T and temperatures down to 0.45 K. In both compounds, the perfect $1/\cos\theta$ behavior of the dHvA frequency for angles θ of the applied field up to 70° from the normal to the conducting planes shows the strong two-dimensionality of the Fermi surface (FS). The angle-dependent magnetic-breakdown orbit found in κ-(ET)$_2$Cu(NCS)$_2$ hints at a small warping of the FS. The unusual angular dependence of the dHvA amplitude with up to 4 spin splitting zeros is quantitatively explainable by a $1/\cos\theta$ dependence of the bare band cyclotron-resonance effective mass. This distinctive behavior allows the separation of the mass enhancement due to electron-phonon coupling from the measured cyclotron-resonance effective mass and the estimation of the superconducting transition temperatures with the standard BCS formula, which are in qualitative agreement with the observed values.

I. INTRODUCTION

Since the discovery of the organic superconductor (TMTSF)$_2$PF$_6$ (T_c=0.9 K at 12 kbar) (Ref. 1) in 1979, where TMTSF stands for tetramethyltetraselenafulvalene, almost 40 different organic superconductors have been discovered,[2] and T_c has increased to just below 13 K at 0.3 kbar in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl.[3] Especially, charge-transfer salts based on the electron-donor molecule BEDT-TTF [or ET=bis(ethylenedithio)-tetrathiafulvalene] constitute the largest family of organic superconductors, and are the most promising for even higher T_c. Salts of the type (ET)$_2X$, where X stands for a monovalent anion, are characterized by a layered structure, where sheets of ET molecules form a two-dimensional (2D) conducting plane and the anions X serve mainly as a separation layer.

Progress in the synthesis and in the techniques for growing high-purity organic crystals of the ET family allowed the observation of magnetic quantum oscillations, starting recently with the Shubnikov–de Haas (SdH) effect in κ-(ET)$_2$Cu(NCS)$_2$,[4] followed by a still growing number of other (ET) salts.[5] These experiments revealed important information on the electronic band structure and the Fermi surface (FS) in organic metals. A common feature of all the organic compounds investigated so far is the two-dimensional band structure, i.e., an almost cylindrical form of the FS, which is responsible for unusual properties such as the very large magnetoresistance oscillations in β-(ET)$_2$I$_3$,[6] and a sawtooth form of the de Haas–van Alphen (dHvA) signal in θ-(ET)$_2$I$_3$,[7] as predicted by calculations of a 2D electron gas in a strong magnetic field.[8] The observation of these effects is only possible if the electronic interlayer coupling is much weaker than the intralayer coupling between adjacent ET molecules forming the conducting planes. Nevertheless, this interlayer coupling is strong enough to cause a slightly corrugated cylindrical form of the FS in the simplest assumption resulting in two extremal areas of the FS yielding a beat pattern in SdH or dHvA signals as seen, for example, in β-(ET)$_2$IBr$_2$.[9,10] This warped structure of the FS also results in a distinctive kind of angular change of the beat frequency and the absolute amplitude of the dHvA signal if the field is inclined from the cylinder axis.[11] The angular dependence of the dHvA amplitude, i.e., the increase at θ=15°–25°, in κ-(ET)$_2$Cu(NCS)$_2$, for example, has been thought to be due to a warped FS.[11,12] As we have pointed out already in a previous, shorter work,[13] this assumption is not correct and we will show in the following that the observed effect can be quantitatively explained by the angular change of the effective mass. Here we focus on the dHvA effect in the organic superconductors α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ ($T_c\approx1$ K) (Ref. 14) and κ-(ET)$_2$Cu(NCS)$_2$ ($T_c\approx10$ K),[15] and present a comprehensive overview of our dHvA measurements in these materials. Although several SdH studies exist,[4,16–19] only one dHvA measurement for κ-(ET)$_2$Cu(NCS)$_2$,[20] and, to date, one SdH study for α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ have been reported.[21] We present for both compounds a detailed study of the angular dependences of the extremal area of the FS, of the dHvA amplitude, and of the cyclotron-resonance effective mass. We will discuss in detail the direct observation of spin splitting in α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ and the observed angle-dependent magnetic-breakdown orbit in κ-(ET)$_2$Cu(NCS)$_2$.

II. EXPERIMENT

The high-purity single crystals of κ-(ET)$_2$Cu(NCS)$_2$ and α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ were grown by electrocrystallization with a constant current applied over a few weeks resulting in plate-shaped samples of a few mm side length and smaller thickness.[22] Samples used for the measurements consisted of irregular-shaped plates with an area of

$\sim 0.8 \times 0.8$ mm^2 and a thickness of ~ 0.5 mm. The orientation of the mounted crystals was carefully checked with a four-circle x-ray diffractometer.

The dHvA effect was measured in a ^{3}He cryostat using the field modulation technique. The samples were mounted in a rotatable sample holder in the center of a superconducting magnet providing fields up to $H = 15$ T. For a field orientation perpendicular to the conducting planes ($\theta = 0°$) and at temperatures of 0.5 K in both crystals, the oscillations were visible above ~ 5.5 T. For fields between 10 and 15 T, the dHvA signal of each crystal was measured at more than 70 different angles between $\theta \approx \pm 70°$. The modulation field ($f \approx 74$ Hz) of a few hundred Gauss was applied parallel to the slowly varying field H. The dHvA signal was detected at $2f$ in a pair of compensated pickup coils with a lock-in amplifier and registered and stored in equidistant steps of $1/H$. Fast Fourier transformations (FFT) were made for each field sweep run in order to obtain the dHvA frequency spectrum. The fundamental dHvA frequency F was determined to better than 0.5% by plotting the arbitrary number of the oscillation maxima versus $1/H$. The slope of the fit line obtained by linear regression of these data directly gives the frequency F. The cyclotron effective masses $\mu_c = m_c/m_e$ were obtained by measuring a few periods of the dHvA oscillations for at least eight different temperatures, recovering the dHvA amplitude $M(\theta)$ via FFT and fitting the data to the usual formula $M/T \propto 1/\sinh(\alpha\mu_c T/H)$ with $\alpha = 2\pi^2 k_B m_e/e\hbar = 14.69$ T/K. The dHvA signal was measured with a field-calibrated RuO-SMD resistor in the temperature range between 0.45 and approximately 1.5 K.

III. RESULTS AND DISCUSSION

A. α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$

Two different samples were measured, of which the first one showed only weak oscillations because of the small weight of the sample and the high Dingle temperature of $T_D \approx 1.3$ K. The second crystal on which we will focus in the following was of much better quality with $T_D \approx 0.6 \pm 0.1$ K. Figure 1 shows a typical result of our dHvA measurements between 5 and 15 T. Oscillations of the magnetization with one frequency, $F = 580$ T, proportional to the extremal cross-sectional area A of the FS ($A = 2\pi eF/\hbar$), are clearly visible starting at 6 T. The Fourier transform of the data between 10 and 15 T, shown in the inset of Fig. 1, reveals the good signal-to-noise ratio of the measurement and the spectral purity of the data. At the angle $\theta = -12°$, where the data were taken, almost no second harmonic at $2F$ is visible.

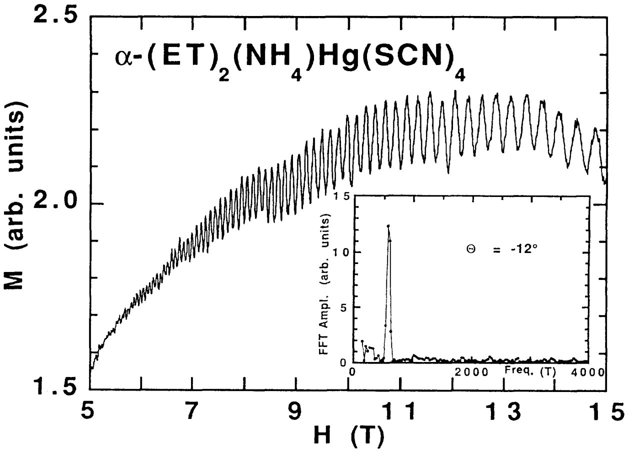

FIG. 1. Magnetization of α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ vs magnetic field, applied at an angle of $\theta = -12°$ normal to the conducting planes. The inset shows the FFT of the data between 10 and 15 T.

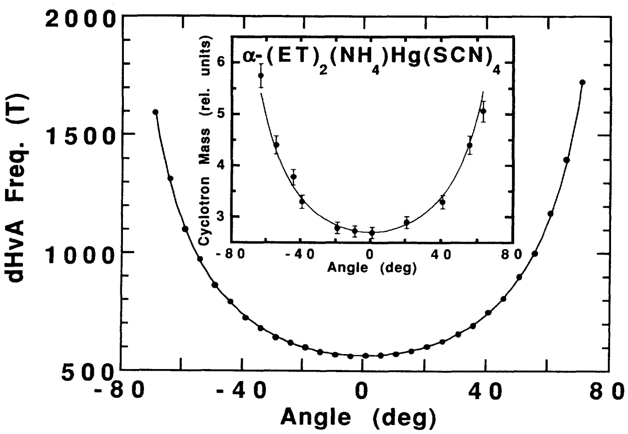

FIG. 2. Angular dependence of the dHvA frequency in α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ with the solid line showing the $1/\cos(\theta)$ behavior. An angle of $\theta = 0°$ means H is normal to the conducting planes. The inset shows the angular dependence of the cyclotron effective mass $\mu_c = m_c/m_e$ with the fit curve obtained using Eq. (2).

We were able to measure dHvA oscillations in α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ for field angles θ between $-71°$ and $+71°$. Figure 2 shows the measured angular dependence of the fundamental dHvA frequency F. The data follow perfectly the behavior $F = F_0/\cos(\theta)$, shown by the solid line, as expected for a cylindrical FS. The minimum frequency $F_0 = 566.7 \pm 1$ T is in agreement with a previous SdH study reporting $F_0 \approx 560$ T.[21] Although no band-structure calculations are available for this compound, the electronic structure should look similar to that of α-(ET)$_2$KHg(SCN)$_4$, where a closed orbit with an area close to the observed value has been predicted[23] and experimentally observed.[24] While the dHvA frequency shows a behavior expected for a 2D electronic structure, dramatic effects in the dHvA amplitude $M(\theta)$ were observed. As an example, Fig. 3 shows the oscillating part of the magnetization at $\theta = 26°$ (the same behavior has been found for $\theta = -26°$) between 10 and 15 T versus the inverse of the field. The absolute amplitude of the oscillation is now reduced compared to the data of Fig. 1 by a factor of ~ 8. The Fourier transform, although with a somewhat reduced signal-to-noise ratio, clearly reveals two peaks. The first peak at $F_1 \approx 630$ T corresponds to the fundamental dHvA frequency expected from the $1/\cos(\theta)$ dependence of Fig. 2. The second, larger, peak at exactly

$2F_1$ does not belong to a new orbit, but is the second harmonic of the fundamental. Obviously, at this angle the spin-splitting factor $\cos(r\pi g\mu_b/2)$ in the Lifshitz-Kosevich formula[25] (g is the spin g factor averaged over a cyclotron orbit and $\mu_b = m_b/m_e$ is the band-structure effective mass in relative units) is close to zero for the fundamental ($r=1$) and, consequently, maximal for the second harmonic ($r=2$). The observed maxima in the measured magnetization oscillations at $\theta = 26°$ can be ascribed to two sets of Landau levels separated in energy by $\Delta\varepsilon = \frac{1}{2}g\beta_e H$, with $\beta_e = e\hbar/m_e c = 2$ Bohr magnetons. The Landau levels themselves are separated by $\hbar\omega_c$. Therefore, the measured magnetization is the superposition of two sets of oscillations shifted by $\Phi = 2\pi\Delta\varepsilon/\hbar\omega_c$ yielding the above-mentioned spin-splitting factor.

From the observed direct spin splitting shown in Fig. 3, we can extract more information about $g\mu_b$. The field H, where the Landau level n just crosses the FS, is given by[25]

$$F/H = n + \gamma \pm \tfrac{1}{2}S \,, \tag{1}$$

where the phase constant γ is normally close to $\frac{1}{2}$ and the spin-splitting parameter is defined as $S = \frac{1}{2}g\mu_b$. Plotting the number of the Landau level versus the corresponding inverse field, shown in the upper part of Fig. 3, yields by linear regression of the data an average frequency for both sets of $F = 627.0 \pm 1$ T. The difference of the intercepts of the fit lines at $F/H = 0$ directly gives $S = 2.43 \pm 0.1$. Because of the ambiguity of the correct assignment of the Landau level number to the respective magnetization maximum, without further information the stated value of S is arbitrary. Actually, as can be seen easily,[25] every value fulfilling the condition $S = r \pm S_0$ with $S_0 = 0.43 \pm 0.1$ would fit our data. Nevertheless, from ESR measurements,[14] the g value is known to be close to 2, and as we will see later, the effective mass μ_b is approximately 2.5 at this angle, resulting in $S \approx 2.5$ and showing the correct assignment of the Landau level numbers in Fig. 3. The phase constant then results in $\gamma = 0.54 \pm 0.1$ in accordance with the expected value of 0.5.

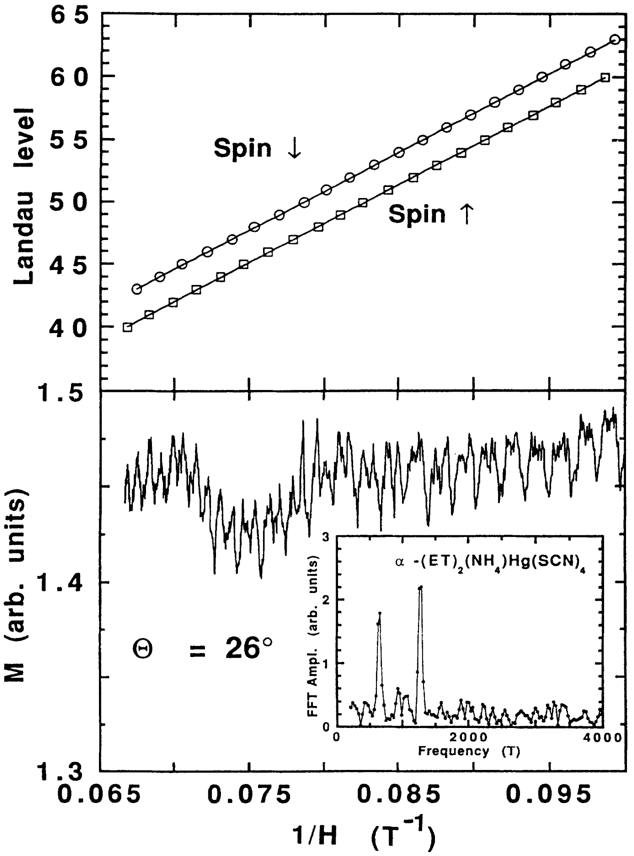

FIG. 3. The lower part shows the magnetization of α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ vs the reciprocal field at $\theta = 26°$. The inset shows the FFT of the data. The upper part shows the number for the two sets of Landau levels for spin parallel and spin antiparallel to the applied field. The solid lines are linear fits of the data yielding a dHvA frequency $F = 627 \pm 1$ T.

Inclining of the field to larger angles θ, the amplitude of the fundamental dHvA frequency in α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ shows three additional maxima and zeros. In Fig. 4 the measured harmonic ratio (HR) of the fundamental M_1 to the second harmonic M_2 is plotted as the solid dots versus θ. At angles where the second harmonic was not clearly observable, as, for example, in the data shown in Fig. 1 and at angles greater than ±50°, the noise level of the FFT was taken as an upper limit for this amplitude, consequently, underestimating the HR at these angles. The points with vanishing M_1 show up as minima (e.g., at ±26°) and those with vanishing M_2 as maxima (e.g., at −12°) in the HR. Obviously, in α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ the spin-splitting parameter S, i.e., either g or μ_b, is strongly angular dependent. From ESR measurements[14] only a slight decrease of ~0.5% of g with angle was found suggesting the effective mass to be the changing part.

The bare-band mass is given by $m_b = (\hbar^2/2\pi)(\partial A/\partial E)$.

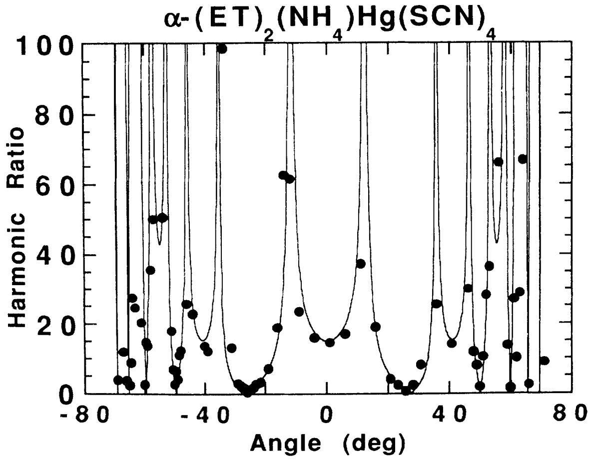

FIG. 4. Angular dependence of the ratio of the fundamental to the second harmonic amplitude of the measured dHvA oscillations for α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$. The solid line represents the harmonic ratio calculated using Eq. (3).

Therefore, the $1/\cos(\theta)$ dependence of the extremal area A of the FS should also be reflected in m_b. To prove this assumption we measured the temperature dependence of the dHvA amplitude to obtain the cyclotron effective mass μ_c, which is the bare-band mass enhanced by electron-phonon interaction. Figure 5 shows a typical result of the effective mass determination for H almost perpendicular to the conducting planes ($\theta=0.85°$). The dHvA amplitude M was measured in the field range 10–10.5 T between 0.46 and 1.3 K. The fit of M/T versus $1/\sinh(\alpha\mu_c T/H)$ results in $\mu_c=2.7\pm0.1$. This value is considerably larger than the value of $\mu_c=2.1$ reported previously from SdH oscillations.[17] The reason for this discrepancy is not yet clear. Nevertheless, in view of the following further analysis of our data, the latter value seems to be rather small. The angular dependence of μ_c, measured at 11 different angles up to $\theta=\pm63°$, is shown in the inset of Fig. 2. A fit of the data using the function $\mu_c=\mu_0/\cos(\theta)$ deviated somewhat from the measured masses near $\theta=0°$. Therefore, a second fit of the form

$$\mu_c(\theta)=\mu_{b0}/\cos(\theta)+\mu_{e\text{-ph}} , \qquad (2)$$

resolving the mass into band structure, $\mu_b=\mu_{b0}/\cos(\theta)$, and an electron-phonon contribution, $\mu_{e\text{-ph}}$, was made. This better description of the data with $\mu_{b0}=2.23\pm0.1$ and $\mu_{e\text{-ph}}=0.5\pm0.1$ is shown in the inset of Fig. 2 as the solid line. Now it is straightforward to explain the observed angular dependence of the dHvA amplitude and the measured HR. From the standard Lifshitz-Kosevich formula, the HR can be easily derived:[25,26]

$$\frac{M_1(\theta)}{M_2(\theta)}=\left|\frac{\cos(\pi g\mu_b/2)}{\cos(\pi g\mu_b)}\right|\frac{2\sqrt{2}\cosh(\alpha\mu_c T/H)}{\exp(-\alpha\mu_c T_D/H)}\times\frac{J_2(2\pi Fh/H^2)}{J_2(4\pi Fh/H^2)} , \qquad (3)$$

where T_D is the Dingle temperature, h is the modulation field amplitude, and $J_2(x)/J_2(2x)$ is the ratio of the Bessel functions of second order. The Bessel functions are included in the above formula because of the modulation field method, and in our experiment are always approximately constant at 0.25. From the measured, well-defined, six extremal points of the HR, we obtain conditions for the spin-splitting parameter S, i.e., $g\mu_b=2n-1$ for the HR being zero and $g\mu_b=m-\frac{1}{2}$ for the HR being infinity, with n and m integers. Assuming $\mu_b=\mu_{b0}/\cos(\theta)$, the most probable values for $g\mu_{b0}$ are plotted in Fig. 6 versus θ. With the fit value of $\mu_{b0}=2.23$ obtained above, we get a g value close to 2 slightly increasing with θ ($\sim4\%$ from 0° to 70°) approximated by a linear dependence as shown by the solid line in Fig. 6. With these angular dependences of g and μ_b, with $T=0.5$ K, $H=15$ T, and $T_D=0.6\pm0.1$ K, we get an excellent quantitative agreement of the calculated HR using Eq. (3), shown as the solid line in Fig. 4, and the experimentally obtained values. The value of $H=15$ T, necessary to fit the HR data around 0°, is somewhat large compared to the measured field range between 10 and 15 T. This discrepancy may be explained by the error bar in T_D.

Our experimental determination of both the enhanced cyclotron mass and the bare-band mass from the same set of dHvA data is unusual. The enhanced mass is obtained from the temperature-dependent amplitude in the usual way. The bare-band mass, determined by the spin-splitting factor $\cos(\pi g\mu_b/2)$ appearing in the HR, is found from the fit of the HR to the Lifshitz-Kosevich form. This procedure is facilitated by the almost constant g factor nearly equal to 2 and by the simple $1/\cos(\theta)$ angular dependence of μ_b.

With the measured values of the effective mass and using the simplest form of the BCS formula, $T_c\approx1.14\theta_D\exp(-1/\lambda)$, we can estimate the superconducting transition temperature of α-$(\mathrm{ET})_2(\mathrm{NH_4})\mathrm{Hg(SCN)_4}$. Calculating the coupling parameter λ through $m_c=m_b(1+\lambda)$ at 0°, we obtain $T_c\approx2.6$ K using the Debye temperature value of $\theta_D=230$ K obtained from specific-heat measurements.[27] This estimate is in the right range of the experimentally observed T_c of

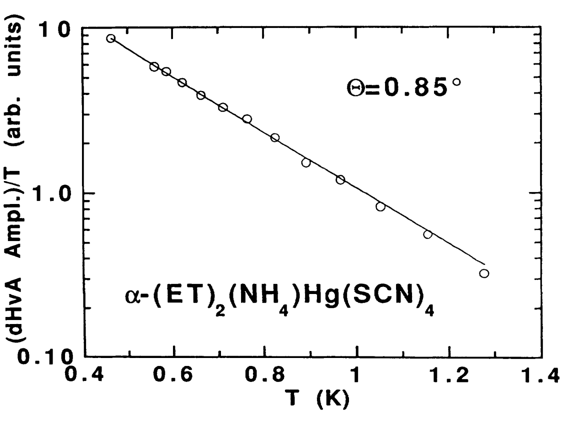

FIG. 5. Logarithmic plot of the amplitudes M of the dHvA signal divided by temperature vs temperature. The solid line shows the fit using $M/T\propto1/\sinh(\alpha\mu_c T/H)$ resulting in $\mu_c=2.7\pm0.1$.

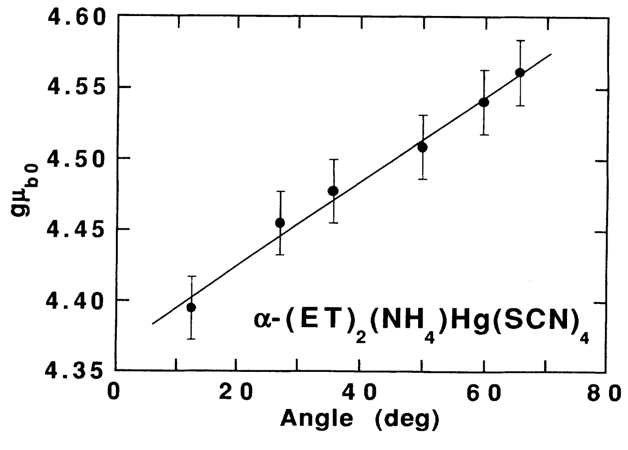

FIG. 6. Angular dependence of the g factor multiplied by the bare-band mass at $\theta=0°$ assuming a $1/\cos(\theta)$ dependence of μ_b. The solid lines show the linear fit of the data.

~ 1 K, but has, of course, large error bars through the exponential dependence of T_c on λ.

Our analysis is based on the Lifshitz-Kosevich expression for a 3D FS, i.e., one with enough curvature for a well-defined extremal orbit to exist. An alternative formulation for an ideal 2D FS,[8] where the cross-sectional area of the FS is effectively constant along its length, gives sawtoothlike oscillations with much larger harmonic content than we observe. There are two conditions for the sawtooth oscillations: the variation in cross-sectional area of the FS must be less than the difference in area of successive Landau tubes in k space, and the Landau levels must be either full or empty, but never partially full. Resistivity measurements of α-$(ET)_2(NH_4)Hg(SCN)_4$ at constant field show an angle-dependent structure[21] which could be explained by a slight warping of the cylindrical FS.[11,28] However, this warping must be less than ~0.5% of the FS cylinder diameter, otherwise a beating pattern of the dHvA signal as seen, e.g., in β-$(ET)_2IBr_2$ (Refs. 9 and 10) would have been observed. Therefore, at fields above ~6 T, the distance between successive Landau tubes is larger than the warped structure, satisfying the first condition for observation of the ideal 2D dHvA oscillations. Apparently, it is the second condition which prevents the observation of the sawtooth oscillations. In α-$(ET)_2(NH_4)Hg(SCN)_4$, there is more than one sheet in the FS producing open orbits not observable in the dHvA effect. These additional sheets provide a reservoir of electrons which establish a chemical potential that is only slightly dependent on the occupation of the Landau levels in the observable closed cylindrical sheet. Thus, as Landau levels on the cylindrical sheet pass through the chemical potential, their occupation changes continuously with field. This violates the second condition and prevents the observation of the ideal 2D sawtooth oscillations.[29]

In the isostructural, nonsuperconducting, organic metal α-$(ET)_2KHg(SCN)_4$ at $\theta=0°$, spin-split SdH oscillations similar to the dHvA signal shown in Fig. 3 were observed.[5,24] The spin-splitting parameter obtained in these reports was $S \approx 1.4$. The measured mass of $\mu_c = 1.4$ and $g \approx 2$ account for this value of S, suggesting that the enhanced mass and the band mass are nearly the same. This would imply that T_c is unmeasurably small and may explain the absence of superconductivity. The spin splitting was observable up to $\theta \approx 15°$ and was not seen at $\theta = 40°$.[5,24] Obviously, in α-$(ET)_2KHg(SCN)_4$ the effective mass is angle dependent and measurements of quantum oscillations over a large angular range could be analyzed in the same way as described above to confirm this conclusion.

B. κ-$(ET)_2Cu(NCS)_2$

The dHvA effect of a carefully aligned sample was measured over a large angular range of ±65°. The magnetization of the sample for the field between 5 and 15 T orientated along a^*, i.e., perpendicular to the highly conducting b-c planes, is shown in Fig. 7. Oscillations appear above 6 T, which is approximately the upper critical field H_{c2} of κ-$(ET)_2Cu(NCS)_2$ at this orientation.[30] The FFT shown in the inset of Fig. 7 reveals the spectral purity of the data at this angle. The dHvA frequency for this field orientation is $F = 598 \pm 3$ T. As in α-$(ET)_2(NH_4)Hg(SCN)_4$, the measured angular dependence of F follows perfectly the 2D behavior $F = F_0/\cos(\theta)$ with the fit value $F_0 = 598.5 \pm 1$ T, plotted as the solid line in Fig. 8. This value is in excellent agreement with the result ($F_0 = 597 \pm 7$ T) from one SdH measurement.[16] Other SdH (Refs. 4,12,17, and 18) studies and one dHvA (Ref. 20) measurement report a frequency between 2 and 10% higher than this value. One SdH study[19] reports two different SdH frequencies with 596±2 and 645±3 T, depending on the current flowing transverse or parallel to H, respectively. This unusual result has not yet been reproduced.[16] The reason for the slight discrepancy between our value of F and those in the literature is not clear, but a larger value of F would be explainable by a slight misalignment of **H**.

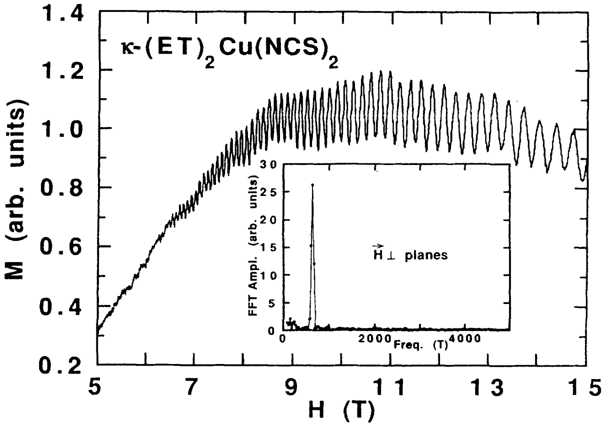

FIG. 7. Magnetization of κ-$(ET)_2Cu(NCS)_2$ vs field applied perpendicular to the conducting planes ($\theta=0°$). The inset shows the FFT of the data between 10 and 15 T.

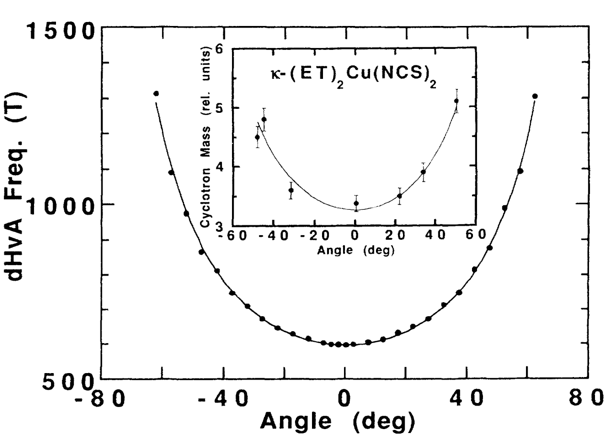

FIG. 8. Angular dependence of the dHvA frequency in κ-$(ET)_2Cu(NCS)_2$ with the solid line showing the $1/\cos(\theta)$ behavior. The inset shows the angular dependence of the cyclotron effective mass $\mu_c = m_c/m_e$ with the fit curve obtained using Eq. (2).

In addition to the fundamental frequency F, we found in the angular range 20°–30° at our highest available fields another frequency F_{MB}. Figure 9 shows an example of the observed behavior at $\theta=-22.7°$, where the higher dHvA frequency of $F_{\mathrm{MB}}\approx 4250$ T is clearly observable in the original data as small wiggles on the dominant low frequency F. In the inset of Fig. 9, the FFT of the data shows F_{MB} together with the fundamental F and the second harmonic $2F$. In the angular range where we could detect F_{MB}, it follows approximately a $1/\cos(\theta)$ behavior which extrapolates to a minimal frequency of $F_{\mathrm{MB}0°}=3940\pm 80$ T at $\theta=0°$. This magnetic breakdown (MB) orbit, and the closed orbit at $F_0=598.5$ T can be well explained by the band-structure calculations.[4] At $\theta=0°$, the MB orbit with a frequency $F_{\mathrm{MB}}\approx 3860$ T has already been reported in two SdH experiments,[16,17] but only at much higher fields, above 20 T. In these experiments, peaks at $F_{\mathrm{MB}}\pm pF$ were seen, in addition to that at F_{MB}, with $p=1,2$. These orbits are only visible due to the quantum interference effect in magnetoresistance measurements,[31] and, as can be seen from the predicted FS,[4] do not correspond to possible dHvA cyclotron orbits.

The MB field is approximately given by[25] $H_{\mathrm{MB}}\approx(H/\hbar\omega_c)(\varepsilon_g^2/E_F)$, where ε_g is the energy gap at the zone boundary and E_F is the Fermi energy. Therefore, the unusual angular dependence of the occurrence of MB hints a k-dependent energy gap, i.e., some kind of structure of the FS of κ-(ET)$_2$Cu(NCS)$_2$. On the other hand, this warping of the FS must for the same reasons as discussed for α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ be less than $\sim 0.5\%$ of the basal area of the FS. An almost smooth cylindrical shape of the FS is also indicated by the absence of structure that was not explainable by the usual SdH effect in the angular dependence of the magnetoresistance in κ-(ET)$_2$Cu(NCS)$_2$.[12] The open sheets of the FS which lead to the MB orbit seem to be the reason why no 2D-like magnetic quantum oscillations were observed in κ-(ET)$_2$Cu(NCS)$_2$ either.

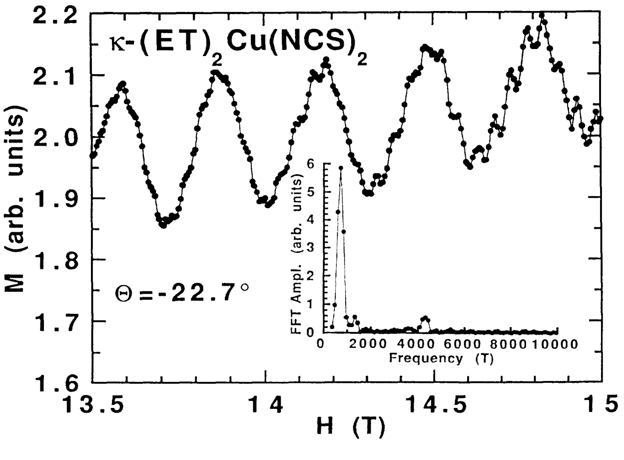

FIG. 9. High-field part of the measured magnetization of κ-(ET)$_2$Cu(NCS)$_2$ at $\theta=-22.7°$ showing the appearance of a higher frequency F_{MB}. The inset shows the FFT of the data with a peak at $F_{\mathrm{MB}}\approx 4250$ T.

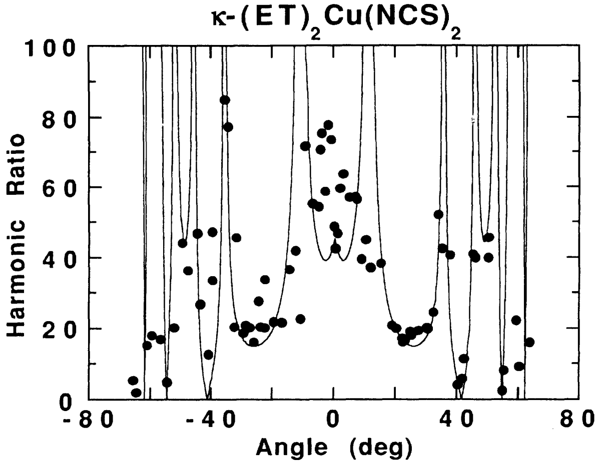

FIG. 10. Angular dependence of the harmonic ratio in κ-(ET)$_2$Cu(NCS)$_2$ with the calculated line using Eq. (3).

Similar to the behavior described above for α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$, we also found in κ-(ET)$_2$Cu(NCS)$_2$ unusual angular changes of the dHvA amplitude. The HR for the measured angles is shown in Fig. 10. Up to $\theta\approx\pm 12°$ in the transformed data, no second harmonic, M_2, was detectable. Therefore, the points in this angular range shown in Fig. 10 are obtained using the noise level of the data as an upper limit of M_2, showing, consequently, a considerable amount of scattering. At $\theta\approx 20°-25°$, the dHvA amplitude was maximal both for the fundamental and the second harmonic, and at $\theta=41.8°$ and 54.8° we found clear minima of the dHvA fundamental.

In order to understand this behavior of the HR in analogy to α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$, we also measured for κ-(ET)$_2$Cu(NCS)$_2$ the angular dependence of the cyclotron effective mass μ_c. The result is shown in the inset of Fig. 8. The value of $\mu_c=3.3$ at $\theta=0°$ is in good agreement with the values reported in different studies presumably done for this angle.[4,16–20] The solid line in the inset of Fig. 8 shows the fit according to Eq. (2) with $\mu_{b0}=2.9\pm 0.3$ and $\mu_{e\text{-ph}}=0.4\pm 0.3$. Using Eq. (3), these values are not consistent with the measured HR and the g value of ~ 2 obtained by ESR measurements.[15] However, adjusting μ_{b0} to 2.6 resulting in $\mu_{e\text{-ph}}=0.7$ gives good agreement with the HR and $g\approx 2$ shown as the solid line in Fig. 10 ($T_D=0.5\pm 0.1$ K, $T=0.5$ K, $H=15$ T). These values of μ_{b0} and $\mu_{e\text{-ph}}$ are within the error bars of the values determined from Eq. (2) and the adjustment of μ_{b0} is reasonable because of the larger uncertainty in the data of $\mu_c(\theta)$ compared to those of α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$. The unmeasurably small second harmonic around 0° means $g\mu_b\approx m-\frac{1}{2}$, where, in our case, $m=6$ and $g\mu_b$ is close to 5.5. In order to also fit the measured zero points of the HR, we therefore had to assume that the g factor is slightly decreasing with increasing angle θ consistent with ESR results.[15]

In κ-(ET)$_2$Cu(NCS)$_2$, because of the higher effective mass we could not find direct spin splitting as observed in α-(ET)$_2$(NH$_4$)Hg(SCN)$_4$ and shown in Fig. 3, although, at higher fields and lower temperatures it should, in principle, be visible. In previous studies[11,12] it was suggested that a slightly warped FS was responsible for the increase of the SdH amplitude around $\theta=20°$. With our results it is obvious that this effect is due to the $1/\cos(\theta)$ behavior of the effective mass, and the g factor near 2. The good quantitative agreement between measured and calculated HR using Eq. (3) gives clear evidence for our interpretation of the data. The estimation of T_c using the BCS formula as described above results in $T_c \approx 6$ K for κ-$(ET)_2Cu(NCS)_2$ with a Debye temperature $\theta_D=215$ K.[32] Again, this is in the right range of the measured T_c and qualitatively explains the higher T_c in κ-$(ET)_2Cu(NCS)_2$ compared to α-$(ET)_2(NH_4)Hg(SCN)_4$.

IV. SUMMARY

In conclusion, the organic superconductors α-$(ET)_2(NH_4)Hg(SCN)_4$ and κ-$(ET)_2Cu(NCS)_2$ both show the characteristic $1/\cos(\theta)$ behavior of the extremal area of the FS of a 2D metal. The areas of the FS in the basal planes are in good agreement with 2D band-structure calculations. In κ-$(ET)_2Cu(NCS)_2$, the angular dependent occurrence of MB gives clear indication of a small corrugation of the FS. At certain angles θ of the external-field spin-splitting, zeros were observed in both compounds, and in α-$(ET)_2(NH_4)Hg(SCN)_4$ the spin splitting could be seen directly. This behavior and the angular-dependent dHvA amplitude could be quantitatively explained with a g value near 2 and an effective mass changing like $1/\cos(\theta)$. With our data the electron-phonon coupling constant could be estimated resulting in critical temperatures in qualitative agreement with the observed T_c.

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