Angular Dependence of the Cyclotron Effective Mass in Organic Superconductors

J. Wosnitza, G. W. Crabtree, H. H. Wang, K. D. Carlson, M. D. Vashon, and J. M. Williams
Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois 60439
(Received 20 February 1991)

We report measurements of the de Haas–van Alphen (dHvA) effect in the organic superconductors α-(BEDT-TTF)$_2$(NH$_4$)Hg(SCN)$_4$ ($T_c \approx 1$ K) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ ($T_c \approx 10$ K) in fields up to 15 T and temperatures down to 0.45 K. For the first time, we determine the angular dependence of the cyclotron effective mass m_c, and the orientation of up to four spin-splitting zeros of the dHvA signal. The angular dependence of the amplitude of the dHvA oscillations is quantitatively explained, and the mass enhancement due to electron-phonon coupling is estimated.

PACS numbers: 74.70.Kn, 71.25.Hc, 71.25.Jd

The steady increase of the superconducting transition temperatures T_c in organic synthetic metals, up to about 12.8 K in κ-(ET)$_2$Cu[N(CN)$_2$]Cl at 0.3 kbar [1], and their often unusual physical properties have created growing interest in these compounds. Salts of the type (BEDT-TTF)$_2X$, where BEDT-TTF (abbreviated ET) represents bis(ethylenedithio)tetra-thiafulvalene and X is a monovalent charge-compensating anion, are among the most promising candidates for higher T_c. Progress in the chemical synthesis of these organic charge-transfer salts and growth of very-high-quality single crystals allows the experimental investigation of the Fermi surface via measurements of magnetic quantum oscillations [2]. The number of compounds where quantum oscillations, with sometimes remarkable new phenomena, are observed has continuously increased [3].

These organic superconductors are layered materials and the anions X serve mainly as spacers between the conducting planes formed by the organic ET donor molecules. Therefore, the common feature among all the metals thus far investigated is a (quasi-) two-dimensional almost cylindrical Fermi surface, which causes the extremal areas of the Fermi surface to vary as $1/\cos\Theta$ [4,5], where Θ denotes the angle between the applied field and the axis normal to the organic molecule layer. The amplitude of the de Haas–van Alphen (dHvA) oscillations, $M(\Theta)$, is determined largely by the enhanced cyclotron effective mass μ_c and the Pauli-spin splitting of the Landau levels, described by a factor $\cos(\pi g m_b/2m_e)$ in the Lifshitz-Kosevich expression, where $\mu_b = m_b/m_e$ is the band-structure contribution to the full cyclotron mass, g is the cyclotron orbital g factor, and m_e is the free-electron mass. Because the band-structure mass μ_b is proportional to the derivative of the cross-sectional area with respect to energy, $\partial A/\partial E$, it varies as $1/\cos\Theta$ just as the areas do. A knowledge of the g factor, the band mass μ_b, and the full mass μ_c allows the amplitude of the dHvA oscillations to be quantitatively explained.

In this Letter we present the first explicit determination of the angular dependence of the cyclotron effective mass m_c, via dHvA experiments in high-quality samples of κ-(ET)$_2$Cu(NCS)$_2$ with $T_c \approx 10$ K [6–8] and α-(ET)$_2$-(NH$_4$)Hg(SCN)$_4$ with $T_c \approx 1$ K [9,10]. For both compounds we report the first observation of spin-splitting zeros, four on the fundamental oscillation in α-(ET)$_2$-(NH$_4$)Hg(SCN)$_4$ and two in κ-(ET)$_2$Cu(NCS)$_2$. By use of a g factor near 2, as measured in ESR experiments, we resolve the measured effective mass into band and electron-phonon contributions, and quantitatively explain the observed dHvA amplitudes as a function of angle. Although several Shubnikov–de Haas (SdH) studies have been reported for these crystals [2,4,5,11–13], there is only one dHvA study previously reported [14].

The dHvA effect was observed by the field-modulation technique at temperatures between 1.5 and 0.45 K. The plate-shaped single crystals, with dimensions of ~ 1 mm diameter and ~ 0.5 mm thickness, were mounted in a rotatable sample holder. The orientation of the crystals was checked with a four-circle x-ray diffractometer. The dHvA signals of each crystal were measured at more than seventy different angles between $\Theta = \pm 70°$ and in fields between 10 and 15 T. Oscillations were visible starting between 5–6 T for Θ near 0° and temperatures at ~ 0.5 K. Each cyclotron effective mass $\mu_c = m_c/m_e$ was determined by measuring three to four periods of the dHvA signal for at least eight different temperatures at a fixed angle. The amplitude of the oscillations $M(\Theta)$ was obtained by fast Fourier transformation (FFT) of the digitized data and then fitted by the usual formula $M(\Theta)/T \propto \sinh^{-1}(\alpha\mu_c T/H)$ with $\alpha = 14.69$ T/K.

The measured angular dependence of the dHvA frequency F, proportional to the extremal cross-sectional area A of the Fermi surface ($A = 2\pi e/\hbar F$), is shown in the insets of Figs. 1(a) and 1(b). The data can be perfectly fitted with $F = F_0/\cos\Theta$, shown as the solid lines in the insets of Fig. 1. For κ-(ET)$_2$Cu(NCS)$_2$ a minimal frequency $F_0 = 598.5 \pm 1$ T is obtained, which is in excellent agreement with the result of SdH measurements from Ref. [4], but (2–5)% less than SdH measurements in Refs. [2, 5, 11, and 12] and dHvA measurements in Ref. [14]. The minimal frequency in α-(ET)$_2$(NH$_4$)-Hg(SCN)$_4$ is $F_0 = 566.7 \pm 1$ T in good agreement with the recently reported value of $1/F_0 = 0.0018$ T^{-1} (no error stated) [13]. Up to the highest measured angles, no detectable deviation from the $1/\cos\Theta$ behavior is found.

The measured cyclotron effective mass μ_c versus angle

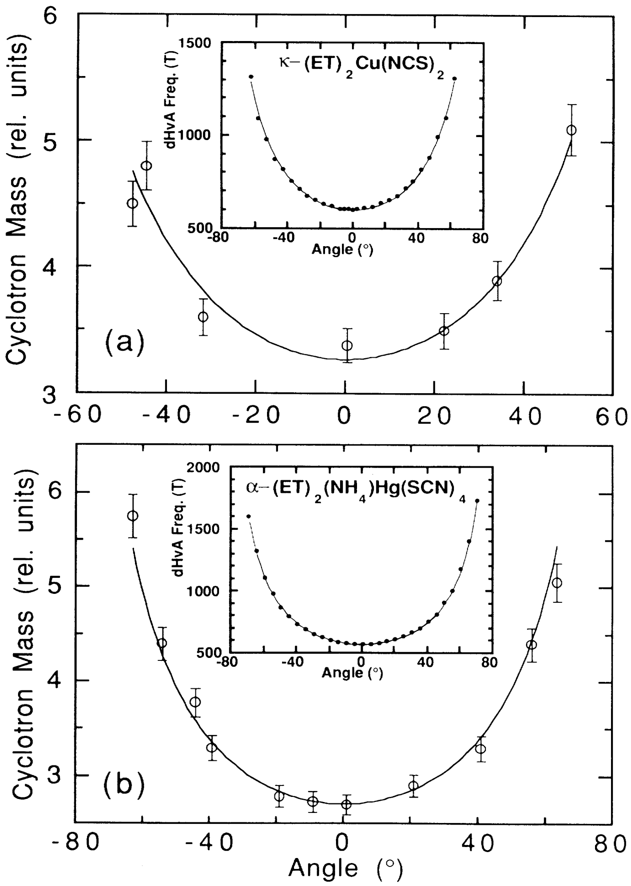

FIG. 1. Angular dependence of the cyclotron effective mass $\mu_c = m_c/m_e$ in (a) κ-$(ET)_2Cu(NCS)_2$ and (b) α-$(ET)_2(NH_4)Hg(SCN)_4$. An angle of 0° means H is perpendicular to the conducting plane. The solid fit curves are obtained using Eq. (2). Insets: The measured angular dependence of the dHvA frequency with the lines showing $1/\cos\Theta$ behavior.

is shown in Figs. 1(a) and 1(b). The value of the measured mass at $\Theta=0°$ for κ-$(ET)_2Cu(NCS)_2$, $\mu_c(0°) \approx 3.4$, is in good agreement with earlier measurements. For α-$(ET)_2(NH_4)Hg(SCN)_4$, we find a larger value, $\mu_c(0°) \approx 2.7$, than was found in the one previous SdH experiment [13]. With increasing angle $|\Theta|$ a clear increase of μ_c can be seen in both compounds. This behavior of μ_c can be understood by the fact that the bare cyclotron mass m_b is defined by

$$m_b = \frac{\hbar^2}{2\pi}\left(\frac{\partial A}{\partial E}\right)_\kappa , \tag{1}$$

with $(\partial A/\partial E)_\kappa$ being the derivative of the extremal area A of the Fermi surface with respect to the energy, keeping the component κ of $\mathbf{k}$ along $\mathbf{H}$ constant. The $1/\cos\Theta$ behavior of the extremal area leads to a similar angular dependence for m_c. A quite reasonable fit of our data is obtained using the function $\mu_c = \mu_0/\cos\Theta$ with values of

TABLE I. Parameters described in the text for the two investigated organic superconductors $(ET)_2X$.

Anion X	μ_0	μ_{b0}	μ_{EP}	T_D (K)
$Cu(NCS)_2$	3.24 ± 0.2	2.9 ± 0.3	0.4 ± 0.3	0.55 ± 0.1
$(NH_4)Hg(SCN)_4$	2.53 ± 0.1	2.23 ± 0.1	0.5 ± 0.1	0.6 ± 0.1

μ_0 shown in Table I. However, the measured masses for α-$(ET)_2(NH_4)Hg(SCN)_4$ deviated somewhat from the fit near $\Theta=0°$, and, for analyzing the spin-splitting effects, a resolution of the mass into band structure (μ_b) and electron-phonon contribution (μ_{EP}) is needed. Therefore, we made a second fit of the form

$$\mu_c(\Theta) = \mu_{b0}/\cos\Theta + \mu_{EP} . \tag{2}$$

This fit is shown in Figs. 1(a) and 1(b) and summarized in Table I.

The measured amplitude of the dHvA signal varied with angle in an unusual way. In κ-$(ET)_2Cu(NCS)_2$, we found maxima in the range $\Theta = 15°–25°$ as has been reported earlier [4,5,15], and zeros at $\Theta = 41.8°$ and 54.8°. In α-$(ET)_2(NH_4)Hg(SCN)_4$, the fundamental nearly vanished at $\Theta = \pm 26°$, leaving an observable second harmonic [16], a pattern that has been seen previously [3,17] and interpreted as a direct observation of Pauli-spin-splitting effects. At higher angles, three additional maxima and zeros of the signal were seen. In order to quantify the angular dependence of the amplitude, we derived the fundamental and second-harmonic dHvA components using FFT. The harmonic ratio (HR) of the fundamental to the second harmonic is plotted in Fig. 2 as the solid circles. At angles above $\pm 50°$, where the second harmonic was no longer clearly observable, the noise level of the FFT was taken as an upper limit for this amplitude, therefore underestimating the HR above these angles.

The HR technique, well known for spin g-factor determinations [18] is based on the expression [18,19]

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

with T_D being the Dingle temperature, h the amplitude of the modulation field, and $J_2(x)$ the Bessel function of second order. The ratio of the Bessel functions, which was always constant at ~ 0.25, has to be taken into account, because of the field-modulation method. It is important to note that the argument $g\mu_b$ occurring in the spin-splitting factor does not depend on electron-phonon interactions [19,20]. The HR is zero where the fundamental vanishes, i.e., for $g\mu_b = 2n-1$, and infinity where the second-harmonic vanishes, i.e., for $g\mu_b = m - \frac{1}{2}$. From the six experimentally, clearly observable extremal

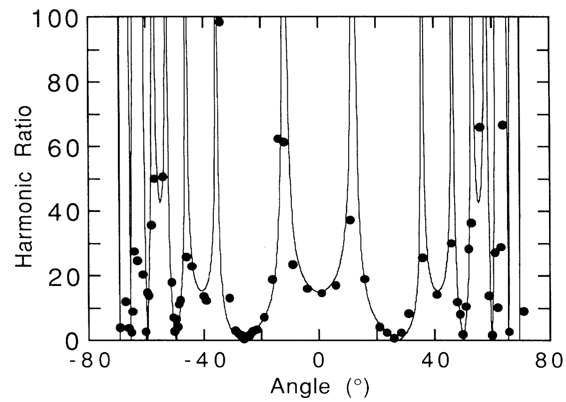

FIG. 2. Harmonic ratios of the fundamental to the second-harmonic amplitude of the measured dHvA oscillations vs angle for α-$(ET)_2(NH_4)Hg(SCN)_4$. The solid line shows the ratio calculated via Eq. (3).

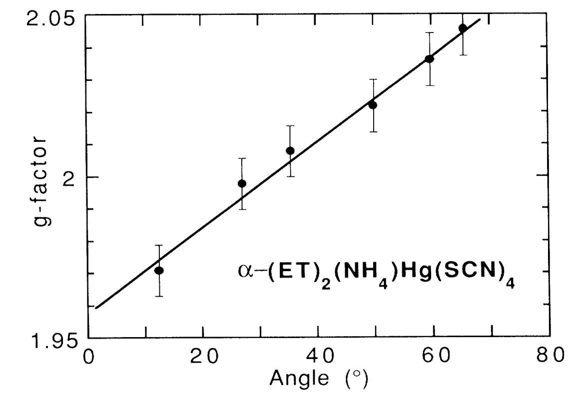

FIG. 3. Angular dependence of the g factor of α-$(ET)_2$-$(NH_4)Hg(SCN)_4$ with linear approximation.

points (zeros of M_1 or M_2) of the HR in α-$(ET)_2$-$(NH_4)Hg(SCN)_4$ and taking $\mu_b = \mu_{b0}/\cos\Theta$, we obtain values of $g\mu_{b0}$ between 4.4 and 4.56. If we assume a negligible electron-phonon interaction, i.e., $\mu_{b0} = \mu_0$, the spin g factor would be $g \approx 1.77$. This is in conflict with the g value of ~ 2 obtained by ESR measurements [10]. However, with the resolution of the measured mass into μ_b and μ_{EP}, we take $\mu_{b0} = 2.23$ and find g factors near 2 shown in Fig. 3. The slight increase of g vs Θ of $\sim 4\%$ from 0° to 70° was approximated by a linear dependence. ESR measurements show a slight decrease of $\sim 0.5\%$ of g with angle [10]. Nevertheless, taking the different determination into account, the absolute value of g is very consistent.

The calculated HR, with $T = 0.5$ K, $H = 15$ T, a Dingle temperature $T_D = 0.6 \pm 0.1$ K as found in our sample, and the effective masses obeying Eq. (3), is plotted as the solid line in Fig. 2. The magnetic field H was chosen as an adjustable parameter to obtain the best fit around $\Theta = 0°$. The somewhat large value of 15 T compared to the experimentally applied field between 10–15 T may be due to an underestimation of T_D. Overall, an excellent agreement between the calculated and the experimentally obtained HR is found. Especially the zero and infinity points are well reproduced and now easily understandable. If g had been chosen constant, some of the calculated extremal points would have been shifted slightly from the observed angles.

In κ-$(ET)_2Cu(NCS)_2$ the angular dependence of the HR is not consistent with the ESR g value [21] of ~ 2 and the value $\mu_{b0} = 2.9$ obtained from the fit of the measured cyclotron masses using Eq. (2). However, a slight adjustment of μ_{b0} to 2.6 leads to an excellent agreement with the HR and a g factor of 2. The difference between the values of μ_{b0} determined from Eq. (2) and from the HR is within the error bars of the fit. The dHvA amplitudes determined in this way describe the vanishing points of the fundamental and the large amplitude around 20° (where M_1 and M_2 have maximum values) very well [16]. The value $\mu_{b0} \approx 2.6$ leads to a value $\mu_{EP} \approx 0.7$ in Eq. (2).

This good quantitative agreement between measured and calculated HR using Eq. (3) gives clear evidence that in the materials investigated here the standard Lifshitz-Kosevich formula for the description of the dHvA effect applies. In particular, an increased harmonic content in the FFT which would be caused by, e.g., magnetic interactions [19] was not observed.

The values obtained for μ_{EP} can be used to estimate the superconducting transition temperature by the standard BCS formula $T_c \approx 1.14\Theta_D \exp(-1/\lambda)$. Calculating λ via $m_c = m_b(1+\lambda)$ at $\Theta = 0°$ we obtain $T_c \approx 3$ K for α-$(ET)_2(NH_4)Hg(SCN)_4$ and $T_c \approx 6$ K for κ-$(ET)_2Cu$-$(NCS)_2$ with Debye temperatures $\Theta_D = 230$ K [22] and 215 K [23], respectively. These estimates are in the right range of T_c and qualitatively describe the higher T_c of the latter compound.

In conclusion, we found in the organic superconductors κ-$(ET)_2Cu(NCS)_2$ and α-$(ET)_2(NH_4)Hg(SCN)_4$ a strong angular increase of the effective mass following a $1/\cos\Theta$ behavior. This is explainable by the observed angular variation of the extremal area of the Fermi surface which perfectly follows a $1/\cos\Theta$ form characteristic of these 2D organic metals. With our result, the angular dependence of the amplitude of magnetic quantum oscillations can be explained and the harmonic ratio of measured dHvA signals is quantitatively predictable. Assuming a g factor of ~ 2, as obtained by ESR measurements, our data allow the mass enhancement induced via electron-phonon coupling to be estimated, giving values which are qualitatively consistent with the observed critical temperatures.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences under Contract No. W-31-109-ENG-38. M.D.V. acknowledges partial financial support from Argonne Division of Educational Programs. J.W. would like to thank the Deutsche Forschungsgemeinschaft for financial support.

[1] J. M. Williams, A. M. Kini, H. H. Wang, K. D. Carlson, U. Geiser, L. K. Montgomery, G. J. Pyrka, D. M. Watkins, J. M. Kommers, S. J. Boryschuk, A. V. Strieby Crouch, W. K. Kwok, J. E. Schirber, D. L. Overmyer, D. Jung, and M.-H. Whangbo, Inorg. Chem. **29**, 3272 (1990).

[2] K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, Phys. Rev. B **38**, 938 (1988).

[3] A recent review is given by M. Tokumoto, A. G. Swanson, J. S. Brooks, C. C. Agosta, S. T. Hannahs, N. Kinoshita, H. Anzai, M. Tamura, H. Tajima, H. Kuroda, and J. R. Anderson, in Proceedings of the International Conference on Organic Superconductors, South Lake Tahoe, California, 20–24 May 1990 (Plenum, New York, to be published).

[4] C.-P. Heidmann, H. Müller, W. Biberacher, K. Neumaier, C. Probst, K. Andres, A. G. M. Jansen, and W. Joss, in Proceedings of the International Conference on Synthetic Metals, Tübingen, September 1990 [Synth. Met. (to be published)].

[5] M. V. Kartsovnik, P. A. Kononovich, V. N. Laukhin, R. B. Lyubovskii, and S. I. Pesotskii, Zh. Eksp. Teor. Fiz. **98**, 708 (1990) [Sov. Phys. JETP **71**, 396 (1990)].

[6] H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, and J. Tanaka, Chem. Lett. **1988**, 55.

[7] K. D. Carlson, U. Geiser, A. M. Kini, H. H. Wang, L. K. Montgomery, W. K. Kwok, M. A. Beno, J. M. Williams, C. S. Cariss, G. W. Crabtree, M.-H. Whangbo, and M. Evain, Inorg. Chem. **27**, 965 (1988).

[8] G. Saito, Physica (Amsterdam) **162-164C**, 577 (1989).

[9] T. Oshima, H. Mori, G. Saito, and K. Oshima, Chem. Lett. **1989**, 1159.

[10] H. H. Wang, K. D. Carlson, U. Geiser, W. K. Kwok, M. D. Vashon, J. E. Thompson, N. E. Larsen, G. D. McCabe, R. S. Hulscher, and J. M. Williams, Physica (Amsterdam) **166C**, 57 (1990).

[11] T. Sasaki, H. Sato, and N. Toyota, Solid State Commun. **76**, 507 (1990).

[12] N. Toyota, T. Sasaki, K. Murata, Y. Honda, M. Tokumoto, H. Bando, N. Kinoshita, H. Anzai, T. Ishiguro, and Y. Muto, J. Phys. Soc. Jpn. **57**, 2616 (1988); F. L. Pratt, J. Singleton, M. Kurmoo, S. J. R. M. Spermon, W. Hayes, and P. Day, in *The Physics and Chemistry of Organic Superconductors,* edited by G. Saito and S. Kagoshima (Springer-Verlag, Heidelberg, 1990), p. 200.

[13] T. Osada, A. Kawasumi, R. Yagi, S. Kogoshima, N. Miura, M. Oshima, H. Mori, T. Nakamura, and G. Saito, Solid State Commun. **75**, 901 (1990).

[14] A. G. Swanson, J. S. Brooks, H. Anzai, N. Kinoshita, M. Tokumoto, and K. Murata, Solid State Commun. **73**, 353 (1990).

[15] This maximum at around 15° is already visible in the first SdH measurement of $(ET)_2Cu(NCS)_2$. See Fig. 3 in K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, Synth. Met. **27**, A165 (1988).

[16] J. Wosnitza (unpublished).

[17] M. Tokumotu, A. G. Swanson, J. S. Brooks, C. C. Agosta, S. T. Hannahs, N. Kinoshita, H. Anzai, and J. R. Anderson, J Phys. Soc. Jpn. **59**, 2324 (1990); T. Sasaki, N. Toyota, M. Tokumoto, N. Kinoshita, and H. Anzai, Solid State Commun. **75**, 97 (1990).

[18] D. L. Randles, Proc. Roy. Soc. London A **331**, 85 (1972); G. W. Crabtree, L. R. Windmiller, and J. B. Ketterson, J. Low Temp. Phys. **20**, 655 (1975).

[19] D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge Univ. Press, Cambridge, 1984).

[20] S. Engelsberg, and G. Simpson, Phys. Rev. B **2**, 1657 (1970).

[21] H. Urayama, H. Yamochi, G. Saito, T. Sugano, M. Kinoshita, T. Inabe, T. Mori, Y. Murayama, and H. Inokuchi, Chem. Lett. **1988**, 1057.

[22] B. Andraka, G. R. Stewart, K. D. Carlson, H. H Wang, M. D. Vashon, and J. M. Williams, Phys. Rev. B **42**, 9963 (1990).

[23] B. Andraka, J. S. Kim, G. R. Stewart, K. D. Carlson, H. H. Wang, and J. M. Williams, Phys. Rev. B **40**, 11 345 (1989).