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Shubnikov–de Haas oscillation with unusual angle dependence in the organic superconductor κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

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The Shubnikov–de Haas measurement of the organic superconductor κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ yields a rapid oscillation originating from the calculated two-dimensional Fermi surface. In addition, a slow oscillation corresponding to 3.0% of the first Brillouin zone area was observed for a field applied perpendicular to the conducting plane. This oscillation shows an anomalous angle dependence on the magnetic field and corresponds to a three-dimensional Fermi surface rather than a two-dimensional one. [S0163-1829(98)07513-4]

The magneto-oscillatory effects of organic conductors with a two-dimensional (2D) Fermi surface (FS) have been studied extensively in recent years.[1] They include a geometrical oscillatory phenomenon called an angle-dependent magnetoresistance oscillation (AMRO) which provides knowledge of the Fermi wave number of the cylindrical FS, as well as the Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) oscillations. It is noteworthy that the observations are rather consistent with the calculated 2D FS based upon the extended Hückel tight-binding method.

Regarding the SdH oscillatory behaviors, however, not a few unusual features have been observed as slow oscillations; these are oscillations with a large period in the scale of an inverse magnetic field $1/H$, compared to that corresponding to the calculated FS. We can point out the examples in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br,[2,3] β-(BEDT-TTF)$_2$IBr$_2$,[4,5] and θ-(BEDT-TTF)$_2$I$_3$.[6] In κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, the origin of the slow oscillation is conjectured to be due to formation of a superstructure appearing below 200 K.[7] On the other hand, the slow oscillation in the latter two salts is not understood in terms of a 2D cylindrical FS and is open for study, although the possibility attributed to some complicated FS topology was proposed for β-(BEDT-TTF)$_2$IBr$_2$.[4,5]

The organic salt κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, with a κ-type arrangement of dimerized BEDT-TTF donor molecules, is semiconducting at ambient pressure and shows a nonmetal-metal transition under pressure, followed by a superconducting transition. The electronic structure was investigated through the observation of an AMRO under pressure.[8] The observed FS of the salt is rather consistent with the calculated one. In addition to the SdH oscillation in agreement with the calculated cylindrical FS, however, we found a new SdH oscillation with a small frequency, possessing an unusual angle dependence of the field against the axis of the cylindrical FS. In this paper, we report the FS which can be understood in terms of a 3D orientation dependence, in contrast to the calculated one.

Samples were synthesized electrochemically as described elsewhere.[9,10] Platinum wires were attached to the sample with a dimension of $0.9\times0.6\times0.03$ mm^3 with conducting carbon paste, yielding a contact resistance of less than 20 Ω. The in-plane resistance was measured by the standard ac method with a measuring current of 0.1–1.5 mA. Experiments were carried out mainly at 1.5 K, and a magnetic field of up to 17 T was applied using a superconducting solenoid. The sample was pressurized using a small clamp cell filled with Daphne 7373 oil as the pressure medium, and the pressure value at liquid-helium temperature was evaluated by taking into account the decrement by cooling. The calculated FS based upon the extended Hückel tight-binding method using room-temperature crystallographic parameters[9,11] consists of two parts; one is a 1D electronlike sheet and the other is a 2D cylindrical, holelike part. Due to the existence of an inversion center in the unit cell represented by $P2_1/c$ symmetry, the 1D and 2D FS's are connected on the first Brillouin zone (BZ) boundary without a gap between them as is the case for κ-(BEDT-TTF)$_2$I$_3$.[12]

A resistance hump resulting from the nonmetal-metal transition under pressure was shifted toward the high-temperature side with increasing pressure. Under 7.6 kbar, the in-plane resistance of the salt exhibited a metallic temperature dependence in the measured range. The residual resistance ratio (RRR) reached 10^3, indicating the high quality of the used sample. This was supported by the experimental observation of a clear AMRO with amplitude reaching nearly 25% of the background resistance. Figure 1 shows the magnetoresistance for the field perpendicular to the conducting plane under 7.6 kbar at 1.5 K. Two types of oscillation are distinguished: a slow oscillation appearing above $\sim$8 T and a rapid oscillation superimposed on the slow one above $\sim$15 T. When the peak positions of these two oscillations are plotted on the scale of an inverse magnetic field $1/H$, a linear relationship between them is found for each oscillation, indicating that these two oscillations can be identified as SdH oscillations. Fast Fourier transform (FFT) processing shows the frequencies in units of a magnetic field of 120±20 T for the slow oscillation and 3780±90 T for the rapid one as shown in Fig. 2. Any higher harmonic or linear combination of them was not observed. Another peaklike structure was

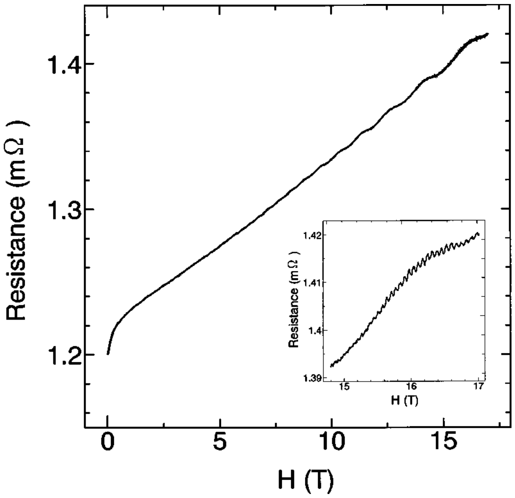

FIG. 1. In-plane magnetoresistance of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ at 1.5 K under 7.6 kbar. The magnetic field was applied perpendicular to the conducting plane. The inset shows the rapid oscillation observed in a high magnetic field range between 15 T and 17 T.

found around ~800 T in the FFT spectrum. We were tempted to assign this oscillation for the 2D holelike α orbit though the oscillation amplitude was rather weak and the frequency was slightly larger than 590 T, the calculated one.

The oscillation frequencies varied with the tilt angle θ of a magnetic field against the normal to the conducting plane as shown in Fig. 3. For the rapid oscillation, SdH signals observed in the angle region ranged from $-20°$ to $+30,°$ obeying the 1/cosθ law. The frequency of 3780 T at $\theta=0°$ corresponds to 97% of the first BZ area calculated by room-temperature crystallographic parameters. The rapid oscillation corresponds to the cylindrical FS called the β orbit, realized by connecting the 1D and 2D parts. This result is in agreement with the FS obtained by the AMRO at the same pressure.

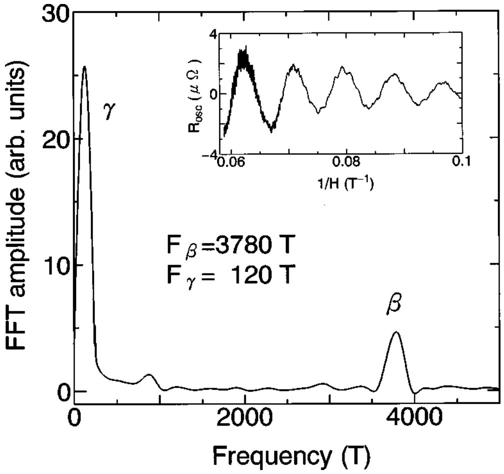

FIG. 2. Fast Fourier transform (FFT) spectrum of the oscillatory component at 1.5 K under 7.6 kbar. The inset shows the oscillatory component obtained from Fig. 1 after a subtraction of a smooth background.

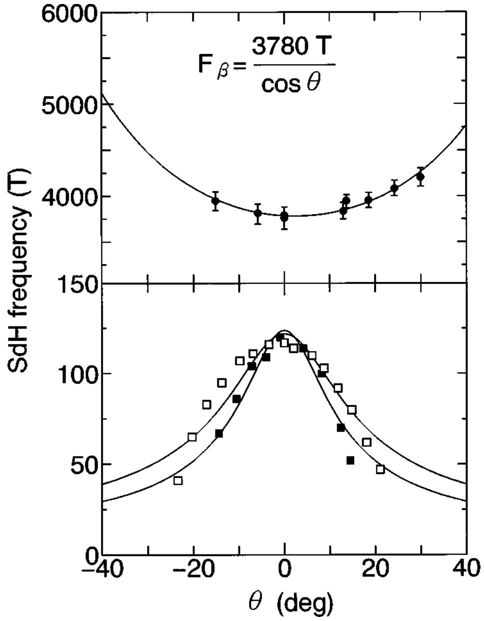

FIG. 3. The tilt angle θ dependence of the SdH frequencies F_β (upper panel) and F_γ (lower panel) observed under 7.6 kbar. The solid line for the upper panel is represented by the denoted equation. In the lower panel, solid and open rectangles denote the angle θ dependence under the azimuthal angle $\phi=150°$ and 90°, respectively, and solid lines are the fit curve assuming an ellipsoidal FS (see text).

In contrast to the rapid oscillation, the SdH frequency of the slow oscillation decreased with the magnetic field tilting from $\theta=0°$. Such behavior was confirmed for the field configurations with $\phi=0°$, 40°, 90°, and 150°, where ϕ denotes the azimuthal angle measured from the c axis in the conducting plane. The slow oscillation for $|\theta|\geqslant 20°$ is obscured due to the limited number of local maxima associated with the undulation as shown in Fig. 4. For instance, at $\theta=-23.4°$ ($\phi=90°$), its oscillation frequency is ~40 T and only three local maxima were observed. At a higher angle with a smaller frequency, we cannot rule out the uncertainty in determining the field corresponding to the resistance peak due to the background magnetoresistance whose behavior changes with the varying tilt angle. It should be noted that the magnetic field up to 17 T used is not strong enough to cover the oscillation with a frequency of less than 30 T. The

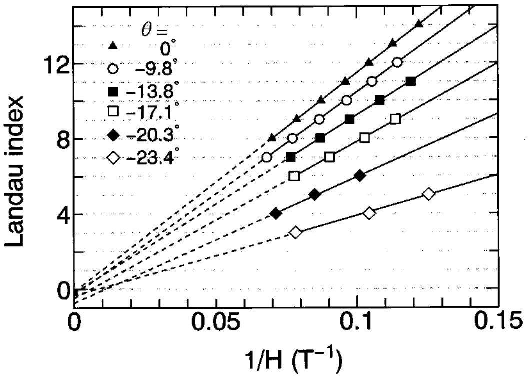

FIG. 4. Landau index vs the inverse magnetic field giving a resistance peak for the slow oscillation at various tilt angles θ under $\phi=90°$. The slope of the solid line provides the oscillation frequency.

cross-sectional area corresponding to the slow oscillation at $\theta = 0°$ is estimated to be 3.0% of the first BZ area, which is only one-fifth of that of the α orbit. Hereafter the relevant orbit is designated as the γ orbit.

From the temperature dependence of the oscillation amplitude, the effective mass can be derived according to a $\ln(A/T)$ versus T relation[13] where A is the oscillation amplitude and T is temperature. Slow and rapid oscillations were observed up to ~4 K and ~2 K, respectively. The estimated effective masses for the β and γ orbits at $\theta = 0°$ were $m_\beta \simeq 4m_0$ and $m_\gamma \simeq 0.5m_0$ where m_0 represents the mass of a free electron.

The angle dependence for the slow oscillation is reminiscent of that observed for the beat frequency ΔF, which results from the existence of the two extremal areas with a similar cross-sectional area.[14,15] It tends to zero with a tilting of the field direction from $\theta = 0°$ to the conducting plane because the beat frequency changes as $\Delta F \propto J_0(dk_{\mathrm{F}}\tan\theta)$,[16] where J_0 is the Bessel function of zeroth order, d is the distance between adjacent conducting planes, and k_{F} is the in-plane component of the Fermi wave vector. However, the oscillatory behavior of the slow oscillation is not of the shape for beating. Thus the oscillation is not a parasitic one but one with a dominating feature as if it is due to a FS with a small cross section.

The slow oscillation with a similar angle dependence was reported for β-(BEDT-TTF)$_2$IBr$_2$.[5] The result was attempted to be explained in terms of a multiconnected FS, where the cylindrical FS's are bridged with complicated thin channels.[4] In such a case, the azimuthal angle ϕ dependence should depend notably upon whether or not the plane formed by varying θ contains the bridging channels. Taking into account the relatively weak ϕ dependence and strong θ dependence, we assume a flat ellipsoid with the shortest diameter along the normal to the conducting plane as a simple model. In this case, the angle dependence of the oscillation frequency, $F(\theta)$, is represented by $1/F(\theta)^2 = (\cos\theta/F_\perp)^2 + (\sin\theta/F_\parallel)^2$ where $F_\perp$ and $F_\parallel$ denote the oscillation frequency at tilt angle $\theta = 0°$ and 90°, respectively. The estimated values of $F_\perp/F_\parallel$ obtained by the fitting are 6.4 and 4.7 for $\phi = 150°$ and 90°, respectively, and the general tendency of the rapid decrease of the frequency is qualitatively explained. However, a discrepancy of the experimental results cannot be neglected as shown in Fig. 3, indicating the complexity of the FS. The presence of a similar 3D FS in layered molecular conductors was reported for θ-(BEDT-TTF)$_2$I$_3$.[6]

Figure 5 shows the pressure dependence of the FS cross-sectional area normalized by the value at 7.6 kbar for slow and rapid oscillations. The AMRO results giving the β orbit are displayed together with the results from the SdH measurement. The pressure dependence for the β orbit is rather consistent with the results for the other κ-type salts.[17,18] On the other hand, the slow oscillation observed above 3.3 kbar shows the pressure dependence represented by $d\ln(S_\gamma)/dP = (4.5 \pm 0.9) \times 10^{-2}$/kbar, where S_γ is the cross-sectional area of the γ orbit. This is several times larger than that for the β orbit and is too large to be understood based upon the empirical tendency that the FS with a smaller cross-sectional area is more sensitive to the applied pressure. Then we consider that the strong pressure dependence may be due to the difference in the origin between the γ orbit and the β orbit based upon the following fact. From an x-ray analysis, we found that there exist shorter contacts between a sulfur atom of the BEDT-TTF molecule and a carbon or nitrogen atom in the anion layer than the sum of each van der Waals radius.[19] This suggests that if the energy levels of highest occupied molecular orbit (HOMO) or lowest unoccupied molecular orbit (LUMO) of the atoms are close to the Fermi energy, a small but finite transfer matrix element between sulfur and carbon or nitrogen may result and form a small FS which is not predicted by the band calculation neglecting the interlayer interaction. Such an interlayer interaction via the anion layer can modify the energy dispersion along the interlayer direction. The strong pressure dependence of the cross-sectional area of the γ orbit may be understood in terms of the drastic enhancement of the transfer integral due to the reduction of the interlayer spacing by pressure.

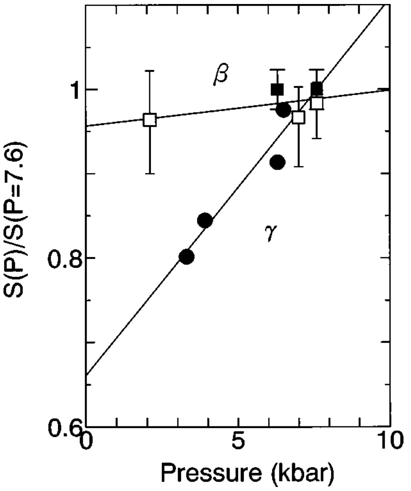

FIG. 5. Pressure dependence of the cross-sectional areas normalized by the value at 7.6 kbar, which are obtained from the SdH oscillation corresponding to the β orbit (solid rectangle) and γ orbit (solid circle), and from AMRO measurements yielding the β orbit (open rectangle). Solid lines show the result of a least-squares fitting.

In summary, we found a new type of slow oscillation in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ under pressure. The angle dependence of the slow oscillation is anomalous in the sense that it has a sharp maximum at $\theta = 0°$ regardless of the azimuthal angle ϕ, indicating that the relevant FS is not two dimensional but three dimensional. It is also noteworthy that the cross-sectional area corresponding to the slow oscillation is much more sensitive to pressure than the 2D cylindrical one. These results may indicate that the electronic role of the anion layers cannot be neglected even if the fraction is not large. This requires that the paradigm of the conventional FS based upon the two-dimensionally aligned π-electron donor molecules should be extended to include the electronic contribution from the anion molecules.

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