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Direct Observation of Spin-Splitting of the Shubnikov-de Haas Oscillations in a Quasi-Two-Dimensional Organic Conductor $(BEDT\text{-}TTF)_2KHg(SCN)_4$

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A clear splitting in the Shubnikov-de Haas oscillation has been directly observed for the first time in a quasi-two-dimensional (2D) organic conductor $(BEDT\text{-}TTF)_2KHg(SCN)_4$. Analysis of the oscillations yields a 2D nature of the cylindrical Fermi surface, corresponding to 16% of the first Brillouin zone, with a small warping along the direction normal to the 2D layer. The condition for observation of spin-splitting and the evolution of the splitting pattern with a tilted magnetic field are discussed.

Recently the Fermi surface study on quasi-two-dimensional (2D) organic metals based on charge transfer salts consisting of BEDT-TTF** molecules has become very popular and several "fermiology" works have been reported such as Shubnikov-de Haas (SdH) effect on $(BEDT\text{-}TTF)_2X$ with $X=Cu(NCS)_2$,[1] I_3,[2,3] IBr_2,[2,4] AuI_2,[5] $AuBr_2$,[6] and de Haas-van Alphen (dHvA) effect on $(BEDT\text{-}TTF)_2X$ with $X=AuI_2$[5] and $Cu(NCS)_2$.[7]

The title compound was reported to show a metallic behavior down to 1.5 K without any superconducting or metal-insulator transitions.[8] It has a layered structure consisting of polymeric anion sheets of $KHg(SCN)_4$ and conducting donor sheets of BEDT-TTF molecules.[8] The anion-sheet thickness (6.8 Å) is much larger than other BEDT-TTF compounds because of its multi-layered structure, so that a strong two-dimensionality due to weak couplings between donor sheets was expected. Accordingly, the conductivity anisotropy (σ_c/σ_b) as large as 2000 at 1.2 K was reported, where σ_c and σ_b are the conductivity along and across the conducting plane, respectively.[9]

Recently, Osada *et al.* measured the high-field magnetoresistance of $(BEDT\text{-}TTF)_2KHg(SCN)_4$ under pulsed magnetic fields up to 40 T, and observed a negative slope above 10 T, a sharp kink structure at 22.5 T, and a large enhancement of the SdH oscillations above the kink structure.[9] Originally, we planned to reproduce the magnetoresistance measurement under the DC magnetic fields up to 23 T, but we found a new aspect in the SdH oscillation waveform, i.e. splitting of each oscillation due to spins, as described below.

In this Letter, we present the first report of a direct observation of the spin-splitting in the SdH oscillations of $(BEDT\text{-}TTF)_2KHg(SCN)_4$ under DC magnetic fields below 23 T, where more than 30 Landau tubes are below the Fermi level. The observation of direct spin-splitting of SdH oscillations in such a condition, i.e. far from the quantum limit, is very unusual and has never been reported so far in organic metals.

Single crystals of $(BEDT\text{-}TTF)_2KHg(SCN)_4$ were grown by electrochemical method.[8] The crystal structure belongs to triclinic with space group $P\bar{1}$, and lattice parameters $a=9.948$ Å, $b=20.505$ Å, $c=9.833$ Å, $\alpha=103.34°$, $\beta=90.53°$, $\gamma=92.80°$, $V=1949$ Å^3, $Z=2$ at 104 K.[8] Typical sample size was $2\times1\times0.5$ mm^3. Conducting 2D layer spreads along the *a-c* plane, which is the most developed crystal face. AC (~13 Hz) resistance measurement were carried out using linear four electrical contacts made of evaporated gold pads with gold electrical leads. The high-field mag-

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** bis (ethylenedithio) tetrathiafulvalene.

netoresistance measurements were carried out in magnetic fields up to 23 T generated by a water-cooled Bitter-type magnetat at Francis Bitter National Magnet Laboratory. The sample attached to a rotatable sample holder was immersed in liquid ^{3}He during the measurements.

Figure 1(a) shows the resistance at 0.6 K as a function of magnetic field applied normal to the 2D plane. From the figure we can see clear SdH oscillations at fields above $\sim$10 T. The overall field dependence of the background magnetoresistance is similar to the report by Osada *et al.*[9] However, we notice a distinct difference in the oscillation waveform. That is, each oscillation has a double peak structure. A straightforward Fourier transform of the data gives us an anomalously large second harmonic at 1350 T, in addition to the fundamental field at 674T as shown in Fig. 1(b). The fundamental SdH frequency, $F=674$ T, corresponds to the cross-section of Fermi surface (FS) $S=0.065$ Å^{-2}, i.e. 16% of the first Brillouin zone (BZ), consistent with the report by Osada *et al.*,[9] in reasonable agreement with the value (19%) given by the band structure calculation.[10] Large and anharmonic SdH oscillations were reported by Kang *et al.*[3] in the high-T_c state of β-(BEDT-TTF)$_2$I$_3$. They attributed these to both the 2D character of the electronic motion and high purity of the sample. In the present case, an oscillation at 1350 T, corresponding to twice as large a FS, cannot be a simple second harmonic, since it has even larger amplitude than the fundamental and we don't see ample harmonics higher than the second. Actually, a closer look into the SdH oscillation waveform reveals that the oscillations consist of uneven double peaks denoted by A and B in Fig. 2(b). These waveforms look very similar to those observed in the case of spin-split quantum oscillations.[11] A crucial difference, however, is that such spin-splitting has normally been directly observed only near the quantum limit.

When the oscillation consists of two contributions from spin-split Landau levels, a simple Fourier transform gives us a misleading result. We should rather apply a technique, called best recursive fit (BRF),[12] in which we fit data consisting of a sum of exponentially damped sinusoids plus noise to a linearly recursive sequence. The BRF analysis of the data from 14 to 23 T tells us the presence of frequencies other than the fundamental and second harmonic. There appear to be two second harmonic frequencies (1352 T and 1373 T) separated by $\Delta F/F\approx 0.015$. Such a long beat would show up only as a broadening of the fundamental. The beating frequency gives us directly the amplitude of warping of the cylindrical FS. The ratio is related with the anisotropy of transfer integrals: $F/\Delta F=\hbar^2 k_F^2/2t_b m_{ac}=(k_F a)(k_F c)t_{ac}/t_b$ where t_{ac} and t_b are transfer integrals along and across the 2D

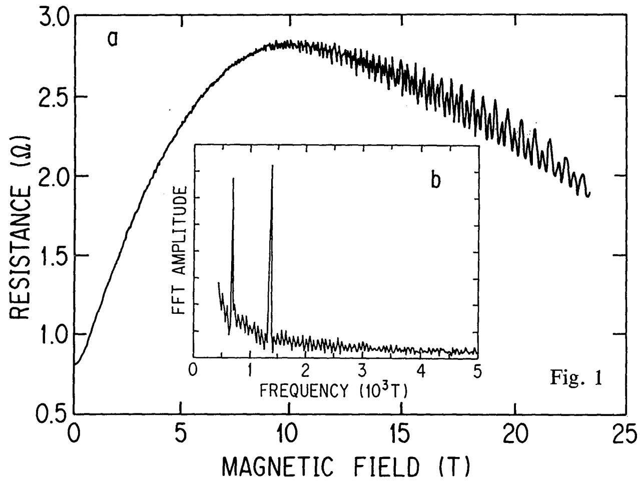

Fig. 1

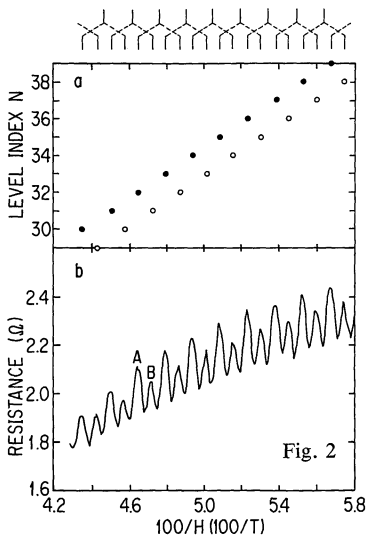

Fig. 2

Fig. 1. (a) The magnetoresistance of (BEDT-TTF)$_2$KHg(SCN)$_4$, under the fields applied normal to the 2D plane ($\theta=0°$). (b) The Fourier transform of the data of (a).

Fig. 2. (a) Plot of level index N vs SdH peaks in reciprocal field. Each alternative peaks were assigned to spin-up (●) and spin-down (○) levels as shown schematically at the top of the frame. (b) The SdH oscillations, as a function of reciprocal field ($\theta=0°$).

plane, respectively. Assuming, for example, a cylindrical FS where πk_F^2 is equal to the experimental value (6.44×10^{14} cm^{-2}) and taking a and c to be lattice parameters, leads to $t_{ac}/t_b = 133$. On the other hand, if we take a typical intermolecular spacing of 3.7 Å instead of lattice parameters, we get $t_{ac}/t_b = 950$. This value is roughly seven times larger than that obtained for β_H-(BEDT-TTF)$_2$I$_3$.[3)]

The spin-splitting of the energy levels in a magnetic field can in favorable conditions be directly observed as a splitting of the oscillations. The conditions are most favorable (1) for oscillations when the components due to spin-up and spin-down levels are out of phase with each other, and (2) for oscillations of as sharp a line shape as possible, and (3) for oscillations of low quantum number, i.e. close to the quantum limit.[11)] In fact, in the case of the needle in Zn, for example, dHvA oscillations of d^2M/dH^2,[13)] and galvanomagnetic oscillations in magnetic breakdown conditions[14)] show this direct splitting as we approach the quantum limit. However, any observable splitting of the oscillations is rapidly masked as H decreases, since the phase separation between up and down spins is independent of H, while the phase smearing due to the other causes varies as $1/H$.[11)]

Let us check if these conditions are satisfied in the present case. The spin degeneracy of the conduction electrons is lifted in a magnetic field, leading to an energy difference between spin-up and spin-down electrons given by

$$\delta = (1/2)g\beta_0 H = (1/2)g(m^*/m_0)\beta H, \quad (1)$$

where $\hbar\omega_c = (e\hbar/m^*c)H = \beta H$ is the Landau level separation. For free electrons, $g=2$ and the spin splitting coincides with the Landau level separation. In real metals, however, spin-orbit coupling and many-body interactions can modify the g-factor and m^* considerably.

The values of $1/H$ for which the Landau tubes just part company with the FS are given by

$$F/H = n + \gamma \pm (1/2)S, \quad (2)$$

where γ is a phase constant which is normally close to 1/2, and $S = (1/2)g(m^*/m_0)$ is spin splitting parameter. Figure 2(a) shows the twenty level indices vs SdH peak positions in reciprocal field. By fitting peaks A and B separately we obtained values of phase constant and spin-splitting parameters as $\gamma = 0.31$ and $S = 1.33$, so that the value of spin-split parameter is close to the value $S = (1/2) g(m/m_0) \approx 1.4$ estimated using g value ($g \approx 2.014$) obtained by ESR measurement[15,16)] and the cyclotron mass $m_c \approx 1.4\, m_0$.[9)] The resulting spin-split energy level scheme is illustrated at the top of Fig. 2(a). Horizontal position of each level corresponds to the value of $1/H$ for SdH peaks in Fig. 2(b). It is to be noted that this configuration obviously satisfies the first condictin, and provides one of the most favorable circumstance for direct observation of spin-splitting in the sense that each level is almost evenly spaced in the energy diagram.

Next, we should examine the second condition, i.e. whether it is appropriate to observe the spin-splitting in the present experimental situation. The spin-splitting would be seen only if the dephasing due to finite temperature and scattering is less than that due to spin up and down. We estimate the energy difference between Landau levels at $H = 16$ T from $\hbar\omega_c \sim 0.9$ meV. From the level scheme, the spacing between adjacent spin-split levels is $\hbar\omega_c/2 \sim 0.45$ meV. The broadening due to finite temperature ($T \approx 0.6$ K) and due to Dingle temperature of our sample ($T_D \approx 0.5$ K)[17)] is calculated from $k_B(T+T_D) \sim 0.3$ meV. We notice that the broadening of Landau levels due to finite temperature and finite relaxation time of the carriers is barely less than the energy spacing between levels. This tells us why the previous report[9)] did not show spin-splitting for a sample with $T_D = 4.0$ K measured at $T = 1.6$ K. Also, as the field is tilted from normal to the 2D plane, the Landau levels are squeezed closer together, and higher effective fields are needed to observe spin-splitting. Figure 3(a) shows the magnetoresistance at 0.6 K for $\theta \approx 40°$, where θ is the angle between the magnetic field direction and the normal to the 2D plane. Note that we do not see the double peak structure any longer. The Fourier transform of the data gives only one frequency at 939 T and no higher harmonics as shown in Fig. 3(b). The fundamental SdH frequency was found to change roughly proportional to the inverse of $\cos\theta$, as expected for a cylindrical FS.

Now what about the third condition? In our experiment, level index tells us that more than 30 Landau tubes still remain inside the FS even at the highest field of 23 T. Thus the magnetic field is not even close to the quantum limit, and it is this crucial point which makes

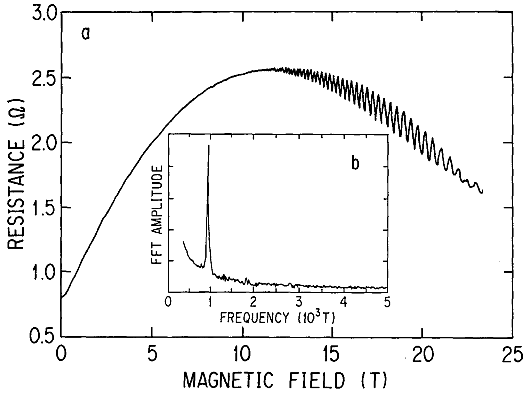

Fig. 3. (a) The magnetoresistance of $(BEDT-TTF)_2KHg(SCN)_4$, under the fields applied about 40° off the normal to the 2D plane ($\theta \approx 40°$). (b) The Fourier transform of the data of (a).

the present observation new and different from the cases reported so far.

Finally, it would be interesting to discuss what happens to the splitting when we tilt the field from normal to the 2D plane. A simple model of the effect of field tilting predicts an appreciable change in the spin-split pattern, since the separation of the Landau levels due to orbital motion depends on the field component normal to the 2D plane, $H_{\perp}=H_{\text{total}}\cos\theta$, while spin-splitting depends on H_{total} and the anisotropy of g-factor which is negligibly small according to the ESR measurement.[16] A preliminary measurement revealed that, contrary to the expectation, the angular dependence of relative position of spin-split peaks is very small at least up to $\theta=15°$. At present, we don't have a good explanation for the discrepancy. Since the SdH frequency changed as $1/\cos\theta$, we suspect that the spin-splitting part is not constant, i.e. g value may be changing as we tilt the magnetic field in contrast to the result given by ESR. The following points about g value[11] could be worthy of further examination. If electron-electron interaction is responsible for departure of g value from the free electron value, the g value obtained by spin resonance is not necessarily the same as the value deduced from SdH oscillations, because electron-electron interactions, although relevant to the energy separation of spin-up and spin-down states, produces an "effective" magnetic field which is always in the same direction as the instantaneous spin magnetic moment, and so can exert no couple on it which will affect the resonance frequency. Also, spin resonance can measure only an average of g over the FS and it is not always obvious how to compare this average with strongly orientation dependent g values deduced from SdH oscillations which average over a particular orbit on the FS.

In conclusion, we report the first direct observation of spin-splitting in the SdH oscillations in a quasi-2D organic conductor $(BEDT-TTF)_2KHg(SCN)_4$. The result suggests that organic metals can be anomalously clean system which enables such observation in a condition far from the quantum limit. The angular dependence of the splitting suggests that the g value anisotropy obtained by spin resonance may not be the same as the value deduced from SdH oscillations.

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