Observation of Giant Magnetoresistance Oscillations in the High-T_c Phase of the Two-Dimensional Organic Conductor β-(BEDT-TTF)$_2$I$_3$

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Giant Shubnikov–de Haas oscillations have been observed in the high-T_c phase (β_H) of the organic conductor β-(BEDT-TTF)$_2$I$_3$. The frequency of the oscillations (H_0=3730 T) corresponds to about one carrier per unit cell. The extraordinary large amplitude of the magnetoresistance oscillations has been attributed to the two-dimensional nature of the cylindrical Fermi surface exhibiting only a small warping along the direction of lowest conductivity.

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Recently discovered organic conductors have provided a significant increase in the superconducting transition temperature (T_c) from ≈ 1 K [in the (TMTSF)$_2X$ family][1] up to about 10 K in the new series of (BEDT-TTF)$_2X$ salts.[2] The β phase of (BEDT-TTF)$_2$I$_3$, abbreviated β-(ET)$_2$I$_3$, is particularly interesting as superconductivity can be observed with two different T_c's at ambient pressure depending on the cooling procedure. When the sample is cooled from 300 K under atmospheric pressure, superconductivity is reached at $T_c \approx 1.5$ K (low-T_c phase, β-L).[3] However, if a small hydrostatic pressure (> 350 bars) is applied while the sample is cooled from 300 K down to about 100 K, and then subsequent cooling to helium temperature is performed under atmospheric pressure, superconductivity is observed at 8.1 K.[4,5] Attempts to study the Fermi surface (FS) of β-(ET)$_2$I$_3$ via the Shubnikov–de Haas (SdH) effect have only been made on the β-L phase. Magnetoresistance oscillations of very small amplitude were observed corresponding to FS cross sections of $\approx 22\%$ of the first Brillouin zone (FBZ).[6] Since we believe that the properties of the β-L phase are strongly influenced by the disorder of CH$_2$ groups acting as scattering centers for the conduction electrons we have undertaken a SdH investigation in the β-H phase using an adequate pressure-temperature treatment. We have found giant SdH oscillations with a frequency of 3730 T. Our data indicate a pronounced 2D character for the FS of β_H-(ET)$_2$I$_3$ with $t_a/t_c \approx 140$. The two dimensionality of the energy dispersion can be responsible for the extraordinarily large amplitude of the magnetoresistance oscillations.

Crystals of β-(ET)$_2$I$_3$ were prepared electrochemically from the BEDT-TTF molecules synthesized by a newly developed procedure.[7] They show clean surfaces and an excellent morphology. Electrical contacts were achieved either by silver paint on preevaporated gold pads or by platinum paint directly applied to the crystals. The sample was oriented by hand under a microscope within an accuracy of several degrees. The resistance measurements were performed with a low-frequency lock-in technique and recorded both digitally and with an analog chart recorder. The digitally recorded data were used for further Fourier analysis. A pressure of up to 1 kbar was generated by a helium-gas technique in a miniaturized Cu-Be cell immersed in a ^{3}He cryostat. The lowest temperature was 380 mK. The temperature was measured and controlled with a germanium thermometer without field and with a capacitance thermometer or home-calibrated RuO$_2$-metal-film resistor in a field. For all experiments, the current was flowing along the direction **a** of highest conductivity and the magnetic field was applied normal to the sample plate (crystallographic a-b plane).

The overall magnetoresistance behavior from 0 to 12 T for two samples is presented in Fig. 1. The SdH oscillations in the high-field region are indicated only by the envelopes because of rapid oscillations. The nonoscillatory part of the magnetoresistance shows an anomaly just above H_{c2}, and a monotonic increase at high fields. SdH oscillations are visible already at 5.5 T at the minimum temperature, but their amplitude decreases rapidly as the temperature increases. The superconducting critical field in our case was ≈ 2 T at 380 mK as compared to ≈ 3.7 T for Bulaevskii, Ginodman, and

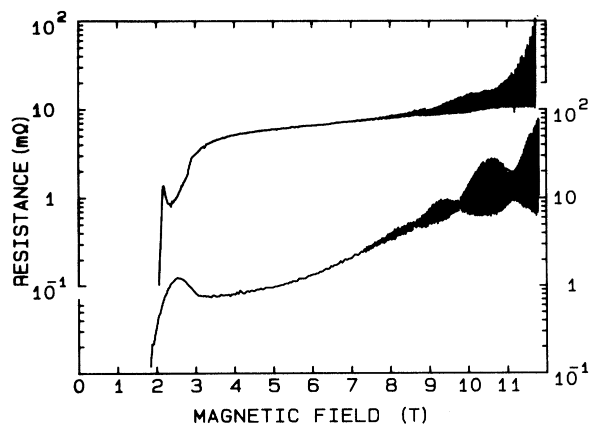

FIG. 1. The overall magnetoresistance behavior of two samples between 0 and 12 T at 380 mK.

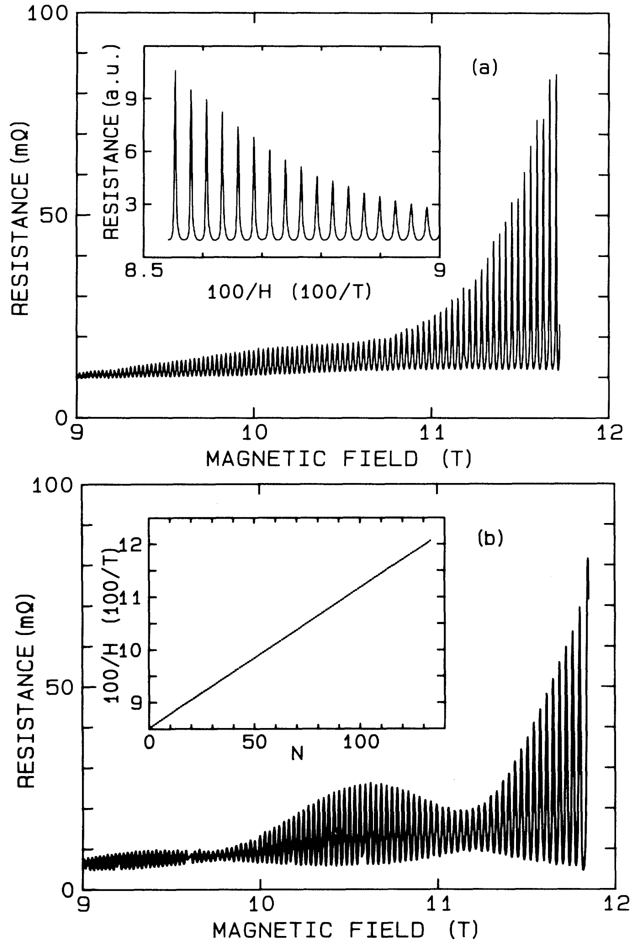

FIG. 2. Details of the magnetoresistance between 9 and 12 T at 380 mK: (a) sample 1; (b) sample 2. Insets: The anharmonicity of oscillations and the linearity of peak positions, respectively.

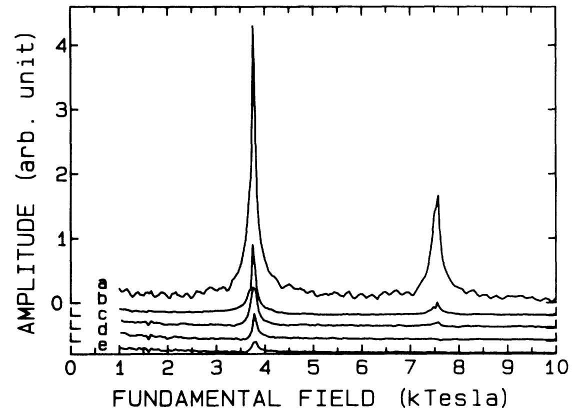

FIG. 3. Fourier transform of experimental data between 9 and 12 T at different temperatures: curve a, 380 mK; curve b, 550 mK; curve c, 700 mK; curve d, 800 mK; and curve e, 900 mK.

Gudenko.[8] Since the critical field is very anisotropic we believe that the a-b plane of our sample was well oriented perpendicular to the magnetic field. In fact, a slight difference in critical fields between samples 1 and 2 is observed (Fig. 1), and the one showing the lower critical field displays larger quantum oscillations. The magnetoresistance behavior at 380 mK for both samples between 9 and 12 T is shown in detail in Fig. 2. In the inset of 2(a) the high-field magnetoresistance at 380 mK is shown on an enlarged scale versus $1/H$ and reveals clearly an enhanced anharmonicity at increasing fields. We also took 133 oscillation peaks and plotted their inverse field values versus integral numbers as shown in the Fig. 2(b) inset. The almost perfect linearity is a test for both the origin of the oscillations and the quality of our data. The slope provides a fundamental field H_0 of 3730 T in very good agreement with the Fourier analysis of the digitally stored data (Fig. 3). The amplitude of the first harmonic decreases exponentially with temperature and that of the second harmonic decreases even more rapidly since its temperature dependence goes like the square of the first harmonic. In general, the dependence of the oscillatory amplitude A of the SdH oscillation on temperature T and field H is expected to have the form

$$A \propto T \exp(-\lambda\mu T_D/H)/\sqrt{H}\,\sinh(\lambda\mu T/H),$$

where $\lambda = 2\pi^2 m_0 c k_B/e\hbar$, $\mu = m_a/m_0$, and T_D is a Dingle temperature. Numerical fitting of our data gives $\mu = 4.65$ and $T_D = 0.53$ K. Admittedly, the determination of the Dingle temperature is somewhat uncertain because of beats. We have only three complete envelopes whose maxima are taken to derive the Dingle temperature. The obtained Dingle temperature is not really consistent with the extraordinary amplitude of the oscillations. Considering $T_D = \hbar/2\pi k_B\tau$, the relaxation time is $\tau = 2.3$ ps. The fundamental field 3730 T corresponds to 3.56×10^{15} cm^{-2} or 51.3% of the FBZ ($S_{BZ} = 6.99\times10^{15}$ cm^{-2}). If the amplitudes of the first harmonic in Fig. 3 at various temperatures are fitted by the standard $\pi\lambda/\sinh\pi\lambda$ formula,[9] which is the Fourier transform of the Fermi function, where $\lambda = 2\pi k T\mu m_0 c/e\hbar H$, then μ is found to be 3.7 ± 0.3 which is consistent with the value quoted above. However, at $T = 0.38$ K, the amplitude of the harmonic is a factor of 2 larger than expected.

There are several features to be pointed out in the magnetoresistance data. One is the appearance of a beat mode when approaching the minimum temperature which means the existence of either two nearby frequencies around the fundamental field or a small pocket of much lower frequency.[6] We could not check the existence of a doublet around the fundamental field because our field limit is not high enough to provide a sufficient resolution in the Fourier analysis. However, from the beat behavior we can derive a frequency $H_1 = 36.8$ T which corresponds to only 0.5% of the FBZ.

The beating can be semiquantitatively explained by a quasi-2D cylindrical FS with a small warping along the k_z direction. Another point to be noticed is the anharmonicity which becomes prominent at 380 mK and at a field greater than 10 T (Fig. 2). As we are far from the quantized regime, this behavior should also be attributed to the typical 2D nature in this compound. (There are still more than 300 Landau tubes inside the FS at 12 T.)

To our knowledge, this is the first time that such large and anharmonic oscillations have been observed with so many Landau tubes inside the FS. This can be attributed to both the 2D character of the electronic motion and the high purity of the sample. SdH oscillations are usually discussed in terms of the density-of-states (DOS) oscillations at the Fermi level and reflect the geometry of the FS. In the usual description of these oscillations for an isotropic FS, the amplitude of the pth harmonic is of the order of $(H/2pH_0)^{1/2}$, where H_0 is the fundamental field proportional to an extremal area of the FS cross section, $H_0 = A_0\hbar/2\pi e$.[9] Let us now consider an anisotropic system with different effective masses m_c along the field and $m_a \ll m_c$ in the plane perpendicular to the field (where we assume an isotropic motion). The amplitude of the oscillations depends on the curvatures of the FS and it is straightforward to show, following the lines of the usual derivation of the DOS, that the harmonics are enhanced by the factor $(m_c/m_a)^{1/2}$. They saturate for a typical field H_1 of the order of $H_0 m_a/m_c$ ($\ll H_0$). Here, we expect m_c to be very large. It is indeed already inferred, from superconducting critical field and conductivity anisotropies, that the ratio of the transfer integrals t_a/t_c is of the order of 40 in this compound.[10] Band calculations corroborate this result and show that the FS is roughly cylindrical with a weak warping along **c**.

A major feature of our magnetoresistance data is the beating of the oscillations which we interpret as due to the two extreme areas of the warped cylinder.[6] The beating frequency gives us directly the amplitude of this warping. We have described the observed features with the following dispersion:

$$E = \frac{\hbar^2 k^2}{2m_a} + 2t_c \cos(k_z c) , \qquad (1)$$

where, for simplicity, we have assumed an isotropic dispersion in the plane of high conductivity. The cross section of the warped FS is modulated as $A_0(k_z) = A_0 + A_1 \cos(k_z c)$ and so is the fundamental field. Instead of Dirac peaks for $A_1 = 0$, the $T = 0$ spectrum in a field consists of a series of Landau bands with square-root singularity of the DOS at the band edges.[11] Their width in energy, $4t_c$, is believed to be larger than the cyclotron frequency $\hbar\omega_c$ and thus the DOS at the Fermi level involves many overlapping Landau bands. The oscillations are described by the two fundamental fields $H_0 + H_1$ and $H_0 - H_1$, where $H_1 = A_1\hbar/2\pi e$, and the ratio H_0/H_1 directly measures the anisotropy of the transfer integrals: $H_0/H_1 = \hbar^2 k_F^2/4t_c m_a = (k_F a)^2 t_a/2t_c$ since $t_a = \hbar^2/2m_a a^2$. Assuming, for example, a cylindrical FS where πk_F^2 is equal to the experimental value (3.56×10^{15} cm^{-2}) and taking a to be a typical intermolecular spacing of 3.5 Å leads to $t_a/t_c = 144$. Since the above formula leads to $H_1/H = 2t_c/\hbar\omega_c$, t_c can also be estimated directly if ω_c, i.e., μ, is known. Taking $\mu = 4$ leads to $t_c = 0.5$ meV and hence to $t_a = 0.07$ eV in fair agreement with other estimates. Note that in this simple model we neglect any possible variation in μ over the FS, which will be inaccurate near the BZ boundary.

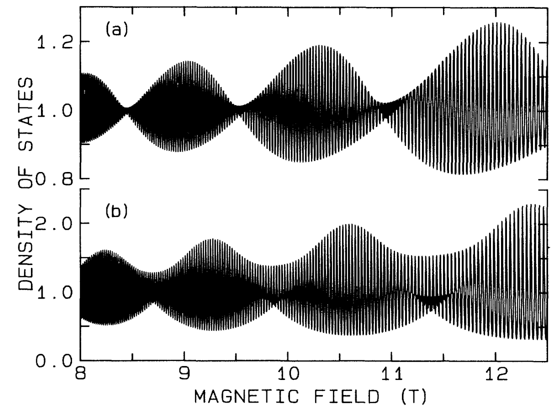

FIG. 4. DOS oscillation of (a) a single cylindrical Fermi surface with a small warping and (b) two perfect cylinders. ($T = 0.38$ K, $T_D = 0$ K, $\mu = 4$, $H_0 = 3700$ T, and $H_1 = 37$ T.)

Assuming the dispersion (1), the following DOS oscillations are derived:

$$n(H) = n(H=0)\left\{1 + 2\sum_p R(p) \cos\left[2\pi p\left(\frac{H_0}{H} - \frac{1}{2}\right)\right] J_0\left(2\pi p \frac{H_1}{H}\right)\right\} , \qquad (2)$$

which, when $H \ll H_1$, reduces to the contribution of the two extreme areas. $R(p)$ is the attenuation factor of the pth harmonics and is the product of at least three functions R_T, R_D, and R_S which describe, respectively, the effects of finite temperature, disorder, and spin splitting. For $\mu = 1$, this equation gives large anharmonicity in a reasonable field (with a scale given by H_1 instead of H_0). But with $T = 0.38$ K and $\mu = 4$, this anharmonicity is strongly reduced and turns out to be smaller than experimentally observed [Fig. 4(a)]. Comparison with experiments suggests several other comments. The envelope of the beating is asymmetric: The maximum of a beating is always to the right of the minimum. This asymmetry, observed experimentally, is due to the special structure of the DOS coming from the asymmetry at the band edge. The amplitude of the nodes of the beatings is not zero. This may have two origins. The first one is the anharmonicity. This gives a peculiar shape of the envelope around the node with different curvatures for lower and upper parts of the envelope, as seen in the experiments (see Fig. 1). The second possibility is that the extreme areas of the tubes lead to slightly different contributions, if the effective mass m_c is different near these two areas. For a more general warping $H(k_z c) = H_0 + H_1(k_z c)$, the Bessel function in Eq. (2) should be replaced by $\langle \cos[2p\pi H_1(\eta)/H] \rangle_\eta$. Indeed when T increases with a concomitant decrease of the anharmonicity, the node is still not well formed which indicates that probably both effects are relevant. The beatings are also probably very sensitive to the field orientation as shown in Fig. 1 where the sample with smaller H_{c2} exhibits larger oscillations.

Our main problem is to understand the large amplitude of the observed oscillations and the observed degree of anharmonicity which are hardly compatible with the estimated μ and T_D. One way to increase these features is to flatten the warping around the extreme areas without reducing the frequency of the beating. This can be achieved by adding harmonics in the variation of $H_1(k_z)$. The extreme situation with two perfect cylinders is shown in Fig. 4(b). In this case the amplitude of the DOS oscillations is larger and approaches that found experimentally in the magnetoresistance; however, the asymmetry of the beatings has disappeared. Furthermore, although there is now some anharmonicity, even in this extreme case it is still much less than that observed experimentally.

In conclusion, we have presented the first observation of giant SdH oscillations with a large fundamental field of 3730 T. The strong 2D character of the energy dispersion in β_H-$(ET)_2I_3$ is responsible for the large amplitude of the effect. We are able to understand the frequency and asymmetry of the beats in terms of the calculated DOS spectrum and a reasonable value of t_c. However, using the same parameters, there are difficulties in accounting for the large amplitude and especially the anharmonicity of the oscillations at the lowest temperature. According to the present picture, at fields $H \sim H_1$ (37 T), gaps should appear in the DOS at the Fermi level.

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