Quantum Oscillations and Negative Magnetoresistance in the Organic Metal β''(BEDT-TTF)$_2$AuBr$_2$

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Shubnikov–de Haas oscillations are observed in the low-temperature magnetoresistance of the organic metal β''(BEDT-TTF)$_2$AuBr$_2$, which indicate the presence of small carrier pockets in the Fermi surface. The nonoscillatory part of the magnetoresistance is highly anisotropic, and in one current direction an anomalously large negative magnetoresistance is observed. Some possible explanations for the negative magnetoresistance are considered, including an explanation based on magnetic-field–induced alignment of the carrier motion in the presence of scattering from internal boundaries.

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Organic metals based on the organic molecule *bis*-(ethylenedithio)-tetrahiafulvalene (abbreviated as BEDT-TTF or ET) are of particular interest since many of them are superconductors with transition temperatures up to 10.4 K.[1] We report here high-field magnetoresistance (MR) measurements on the organic metal β''(ET)$_2$AuBr$_2$ in which we have measured a complex series of Shubnikov–de Haas (SdH) oscillations and observed a giant negative magnetoresistance (NM) for the first time in an organic conductor.

The β''-phase ET compounds have a two-dimensional (2D) layer structure with sheets of interacting ET molecules separated from each other by anion sheets. In contrast to the simple open Fermi surface of the tetramethyltetraselenafulvalene salts,[2] band-structure calculations on the β'' phase suggest that the Fermi surface has two sections, one open and one closed.[3,4] In the case of metals with closed regions of Fermi surface, SdH oscillations in the MR give valuable information about the form of the Fermi surface, which can be used to test models of the band structure.

Crystals of (ET)$_2$AuBr$_2$ were prepared electrochemically, the β'' phase forming as thin distorted hexagonal plates typically $1\times1\times0.1$ mm^3. The triclinic structure of this phase has been reported by a number of authors[3,5,6]; in our cell notation the sheet of ET molecules is in the *a-b* plane with the ET dimers stacked along the *a* axis,[3] but the strongest interaction between the ET is in the interstack *b* direction.[5] Four gold contact pads were evaporated onto the *a-b* face of the crystal in a square pattern, allowing measurements to be made with current flow (j) parallel or perpendicular to the *b* axis and also in Hall geometry. Sample cooling was by a He^3-He^4 dilution refrigerator, giving sample temperatures down to 150 mK. Steady magnetic fields were applied with use of a 20 T Bitter magnet.

At room temperature both conductivity and infrared reflectance studies[4] indicate that direction *b* has higher conductance than direction *a*. When some samples are first cooled, however, it is found that the higher conducting direction switches to the *a* axis at around 100 K; this reversed anisotropy remains on warming to room temperature and on subsequent temperature cycles. This transition occurred in the sample described here. Another sample which did not show resistance reversal on cooling did not display SdH oscillations or NM, presumably indicating a short scattering time. Further work, partic-

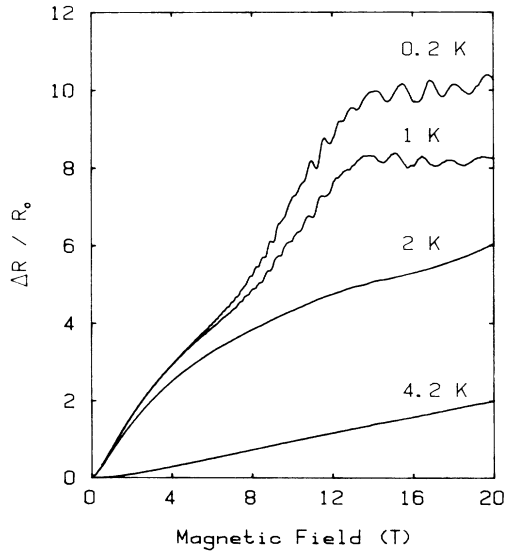

FIG. 1. Transverse magnetoresistance for the high-resistance direction ($j\|b$) with $B\perp(a,b)$.

ularly structural studies at different points in the thermal cycle, is required to understand this unusual behavior.

The MR for j parallel to b, the higher-resistance direction at low temperature by about a factor of 30, is shown in Fig. 1. Oscillations periodic in $1/B$ are visible below 2 K. Fourier analysis of the oscillatory part of the MR reveals three well-resolved frequencies of comparable intensity, with fundamental periods of 140, 190, and 220 T (Fig. 2), together with a much slower oscillation which could not be clearly separated from the background. No Hall resistance could be detected within the sensitivity of our experiment, which is consistent with the large carrier concentration expected from the stoichiometry: We conclude that the observed oscillations are SdH oscillations corresponding to closed orbits with, respectively, 1.7%, 2.3%, and 2.7% of the area of the Brillouin zone derived from the room-temperature structure.

The dependence of the amplitude of A of SdH oscillations on temperature T and field B has the form[7] $A(T,B) \propto \frac{1}{2} B e^{-\zeta} \chi/\sinh\chi$, where $\chi = 14.7(m^*/m_e)T/B$, $\zeta = 14.7(m^*/m_e)T_D/B$, and T_D is the Dingle temperature. The SdH oscillation amplitudes shown in Fig. 2 are an average amplitude over the sampled range of $1/B$ and this must be taken into account when deriving the effective masses. For the 220-T oscillation we get $m^* = (2.0 \pm 0.3)m_e$ and $T_D \sim 1$ K, indicating a scattering time ~ 10 ps. The 140- and 190-T oscillations are almost independent of temperature up to 600 mK; the weak temperature dependence is indicative of a small effective mass, of order $(0.4\text{–}0.7)m_e$. Above 600 mK the amplitude of the 190-T oscillation falls steadily, while the amplitude of the 140-T oscillation drops between 600 and 800 mK but remains almost constant between 800 mK and 1 K.

The MR for j perpendicular to b is shown in Fig. 3. Oscillations are again visible below 2 K for fields above 15 T. The mean fundamental period is ~ 190 T but insufficient oscillations are observable to distinguish whether more than one period is present in this direction. The most dramatic feature of the MR in this orientation, however, is the very large negative component which is observed at 2 K and below. This NM appears to saturate around 10 T and a positive component takes over at higher fields. The magnitude and form of the NM in this work is similar to that observed in the charge-density-wave phase of $1T$-TaS_2 (Ref. 8) where the temperature-dependent conductivity supports Mott variable-range hopping conduction; the NM was explained by a spin-dependent change in localization length with magnetic field. By contrast, we do not observe the characteristic Mott temperature dependence of the resistance, and furthermore, the high-field oscillatory behavior indicates a sharp Fermi surface. A small NM ($\lesssim 10\%$) has been observed both in $\beta''ET_2AuBr_2$ (Ref. 6) and in other organic metals[9,10]; the effect is observed to be sample dependent and it has generally been attributed to weak localization. The effect here is very large however; at 200 mK the sample loses $\sim 98\%$ of its zero-field resistance at 10 T.

Current theories for NM in metallic systems generally involve a perturbation expansion both in the disordered potential and in the electron-electron interaction.[11] Disorder causes NM since the magnetic field disrupts coherent backscattering and suppresses localization; interaction between electrons also leads to NM if it is at-

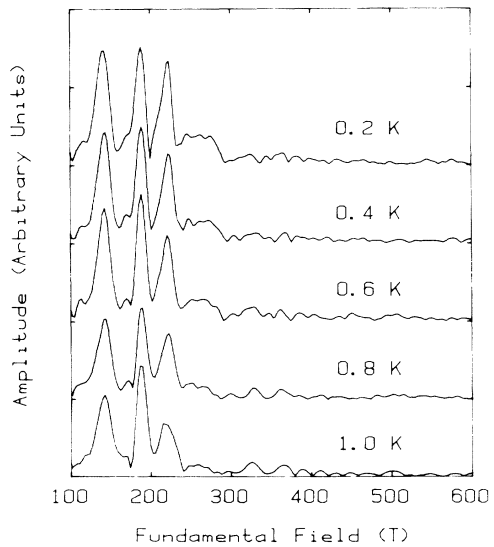

FIG. 2. The fundamental field (frequency) spectrum of the oscillations periodic in $1/B$ derived from the oscillatory magnetoresistance of Fig. 1 by Fourier analysis.

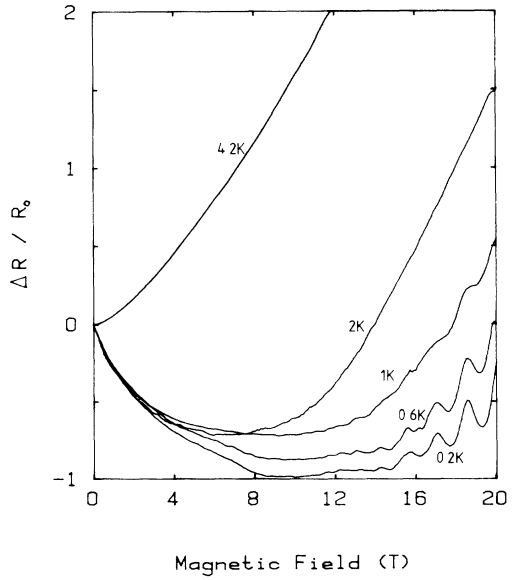

FIG. 3. Transverse magnetoresistance for the low-resistance direction ($j \perp b$) with $B \perp (a,b)$.

tractive and such attractive interactions are likely in view of the existence of superconducting ET compounds. For 2D systems the localization contribution to the MR, $\Delta\rho$, is expected to have the form[12,13]

$$\frac{\Delta\rho}{\rho_0} = -R\Delta G = R\frac{e^2}{\pi h}\left[\ln\left(\frac{B_i}{B_0}\right) + \psi\left(\frac{1}{2}+\frac{B_0}{B}\right) - \psi\left(\frac{1}{2}+\frac{B_i}{B}\right)\right], \quad (1)$$

where ψ is the digamma function, ΔG is the equivalent magnetoconductance, R is the resistance, and B_0 and B_i are characteristic fields which are proportional to the elastic and inelastic scattering rates, respectively. This expression has a logarithmic behavior at high fields. The electron interaction contribution to the MR has the form[14]

$$\frac{\Delta\rho}{\rho_0} = -R\Delta G = R\frac{e^2}{\pi h}g(T,B)\varphi_2\left(\frac{2DeB}{\pi kT}\right), \quad (2)$$

where $g(T,B)$ is the renormalized dimensionless electron-electron interaction (negative for an attractive interaction), D is the diffusion constant, and $\varphi_2(x)$ is a function that behaves quadratically at small x and logarithmically at large x.

While it is possible to use either (1) or (2) to describe the NM for fields below 10 T and for temperatures where the negative component of MR is fairly small, the NM at 0.2 K is too large to be described by such expressions. This is because the sample conductance increases from a zero-field value of $\sim$70 to $\sim$3500 S at 10 T while the scale of the theoretical magnetoconductance from (1) or (2) is of the order of $e^2/\pi h$ ($=1.23\times10^{-5}$ S). Even if we assume that the sample consists of a stack of $\sim10^5$ 2D sheets of ET in parallel (more than accounting for the thickness of the sample), the observed effect is still several orders of magnitude larger than expected from the perturbation treatment of localization or electron interaction.

Before an alternative explanation for this effect is proposed we will establish what can be inferred about the Fermi surface from the SdH oscillations and the nonoscillatory positive component of the MR. If the charge transfer results in one hole per unit cell we expect a band structure with the equivalent of one half-occupied band and a Fermi surface enclosing half the Brillouin zone area. The three SdH periods account for a mere 7% of the Brillouin zone area, suggesting that a large portion of the Fermi surface is open. In view of the resistance anisotropy it is logical to conclude that this Fermi-surface section is open in the b direction. A nonsaturating component of MR is therefore expected for current in this direction. The b-axis MR at 2 K (Fig. 1) appears to have two components, one of which saturates at about 5 T while the other (presumably derived from the open band) continues to increase. In the direction perpendicular to b (Fig. 3) the more usual positive MR overwhelms the NM discussed above at high fields. If there is a 1D orbit open in the b direction we would expect the MR perpendicular to b to saturate at high field. This is not seen at 20 T, possibly because of a large scattering rate in the 1D band. It is not clear why SdH oscillations and positive MR are seen at high field in this direction but this might be due to magnetic breakthrough[15] causing transfer of carriers between the open and closed portions of the Fermi surface.

SdH oscillations in other ET salts have been recently reported.[14,16,17] These materials all have larger orbits taking up $\sim$20% of the Brillouin zone and the β-phase materials also have a smaller pocket ($\sim$2%). In the absence of structural information at temperatures below 100 K, any comparison of our observed oscillations with calculated band structures must be tentative. However, the simple two-band extended Hückel method,[5] besides being rather sensitive to the choice of orbital parameters for the atomic species, seems unlikely to yield a sufficiently rich structure in the Fermi surface, although its prediction of coexisting 1D and 2D orbits at the Fermi energy is borne out in our results. A more complete local density-functional calculation performed on the β phase has shown a more complicated Fermi surface[18] and a similar calculation may be needed to describe the complex β'' Fermi surface.

We now return to the origin of the massive NM. This is observed for current in the direction for which the 1D band is expected to dominate. The effect of an increasing magnetic field on such a band is to sweep carriers

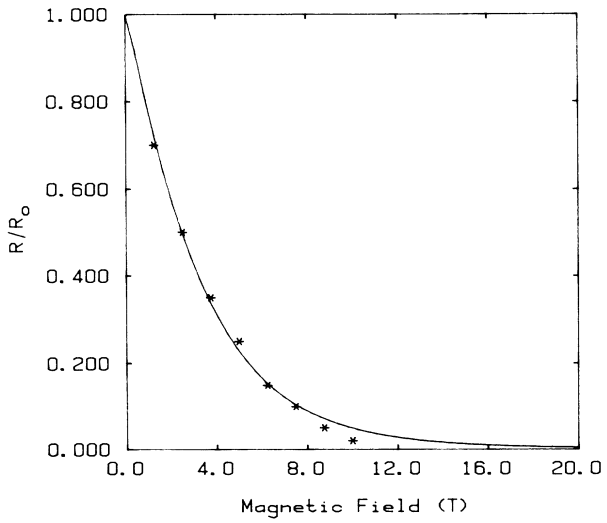

FIG. 4. Data for $j\perp b$ at 0.2 K compared with linear-scatterer theory (solid line) taking the parameter values given in the text.

across the Fermi surface at a progressively faster rate. The corresponding carrier path in real space becomes increasingly closely aligned with the higher conducting a axis and motion in the b direction is effectively quenched by the magnetic field. If the dominant scatterers are in lines parallel to the a axis then the scattering cross section will decrease as the b-axis motion is reduced. Such linear scattering centers might, for example, be due to some form of domain boundary. At high fields, this boundary scattering will vary as $1/B$ and the mean free path will be limited by temperature-dependent inelastic scattering and by scattering from isolated defects. The MR calculated on the basis of this model[19] with parameters chosen to reproduce the 0.2-K data is shown in Fig. 4. The anisotropy of the open orbit was taken as 10:1, the density of linear defects was taken to have a normal distribution about a mean value of 3×10^7 m^{-1}, and the mean free path when avoiding the linear scatterers was taken as 400 μm. It can be seen from Fig. 4 that a mechanism of this kind is capable of accounting for the large observed NM. This large mean free path is comparable to that in single-crystal sodium at 4.2 K, where boundary-related NM was observed.[20] While an explanation of the NM based on localization or electron interaction cannot be ruled out, the absence of any significant temperature dependence of the zero-field resistance below 4.2 K suggests that the linear-scatterer theory is the most likely of the explanations considered.

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