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Pressure-induced nesting in the low-dimensional organic superconductor α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$

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Why superconductivity appears in only one member (M = NH$_4$) of the isostructural family of organic conductors α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ is a long-standing question. Others in the family (M = K,Rb,Tl) have density-wave ground states. To address this problem, we have studied pressure effects in superconducting α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ (T_c = 1.0 K). Our results show a remarkable pressure dependence of the Fermi surface topology. We argue that with NH$_4$, there are small deviations from perfect nesting of the open-orbit bands which favor superconductivity over a density-wave state.

α-(BEDT-TTF)$_2M$Hg(SCN)$_4$, where (BEDT-TTF) is bis(ethylenedithio)tetrathiafulvalene, is a family of quasi-two-dimensional (Q2D) organic conductors (where M = NH$_4$, K, Tl, or Rb)[1,2] of great interest due to their low-temperature properties, which include superconductivity for M = NH$_4$ (an ambient pressure superconductor[3] below 1.0 K) and magnetic (density-wave) phases for the rest of the series. The Fermi surface (FS), which is composed of closed hole orbits and open electron orbits, is expected to be very similar for all four members of the series. The superconducting material α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ exhibits a single Shubnikov–de Haas (SdH) frequency of 568 T in high magnetic fields.[4] In contrast, α-(BEDT-TTF)$_2$KHg(SCN)$_4$,[5] α-(BEDT-TTF)$_2$RbHg(SCN)$_4$,[6] and α-(BEDT-TTF)$_2$TlHg(SCN)$_4$,[7] are not superconducting, but have a magnetic-field- and temperature-dependent phase transition at low temperatures (8, 10, and 11 K, respectively), complex magneto-oscillatory behavior, and anomalies in the background and angular-dependent magnetoresistance. A number of authors have attributed the anomalies, such as the anisotropy of the angular-dependent magnetoresistance[7] and the behavior of the background and oscillatory magnetoresistance[8,9] to the influence of the open orbits. The motivation for this work was to remove the superconductivity in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ with pressure for comparison of its nonsuperconducting properties to those in the other three members of the group. We find that pressure has two effects: first, the superconductivity vanishes with pressure as $dT_c/dP \approx -0.25$ K/kbar and $dH_c/dP \approx -0.010$ T/kbar, and second, a small area closed-orbit band is stabilized above 2 kbar. We also find that even the nonsuperconducting form of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ induced by pressure has magnetotransport properties which are significantly different from the other materials.

The samples used in this experiment were synthesized at the Electrotechnical Laboratory. Electrical leads were attached with gold paint and arranged so as to pass current and measure voltage perpendicular to the (a-c) planes. This configuration avoids ambiguities in the current flow, by effectively measuring the contributions of all planes in parallel. Samples were then placed in a standard quasihydrostatic pressure bomb.[10] We note that the low-temperature pressure is less than the room-temperature pressure by as much as 2 kbar at the highest pressures. The pressures stated in this paper are the low-temperature values, determined by scaling to the data of Thompson.[11] The magnetic field was in all cases perpendicular to the conducting a-c plane, and the sample resistance was measured by conventional four-terminal ac phase sensitive detection. The work was carried out at the Francis Bitter National Magnet Laboratory.

In Fig. 1 we show the low-temperature magnetic-field dependence of the magnetoresistance at sequential pressures, at $T \approx 150$ mK. Here a number of important features are observed. For pressure below 2 kbar, we note the appearance of superconductivity with a critical field of less than 0.10 T. At higher fields, a monotonic rise in background resistance is seen along with the onset of Shubnikov–de Haas (SdH) oscillations, which arise from the closed hole orbits in the material. Above 2 kbar, the superconductivity is suppressed, and an anoma-

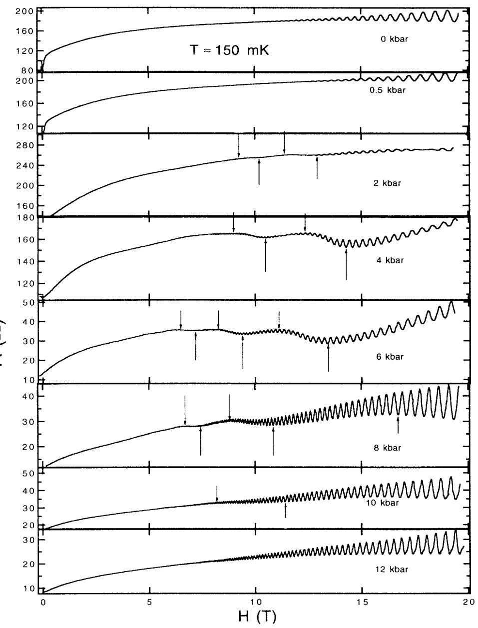

FIG. 1. Magnetoresistance and SdH effect in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ at low temperatures ($T \approx 150$ mK) for different pressures. Note that superconductivity occurs for $P \leq 2$ kbar. The arrows indicate some peaks of the anomalous slow oscillations.

ly in the background magnetoresistance appears. With increasing pressure above 2 kbar, it becomes clear that the anomalies in the magnetoresistance are associated with a new, very small, pressure-dependent closed orbit in the Fermi surface. The arrows in Fig. 1 mark the position of the minima and maxima of these slow oscillations. In Fig. 2, the detailed temperature dependence of both the slow and fast oscillation sequences at 6 kbar pressure is indicated. Here a slight temperature dependence of the slow oscillation magnetic-field positions is apparent, but the fast (hole) oscillation positions do not shift within experimental uncertainties. It should be noted that the slow oscillations are in the range of Landau level index $\nu = 1-5$, the quantum limit, whereas the fast oscillations

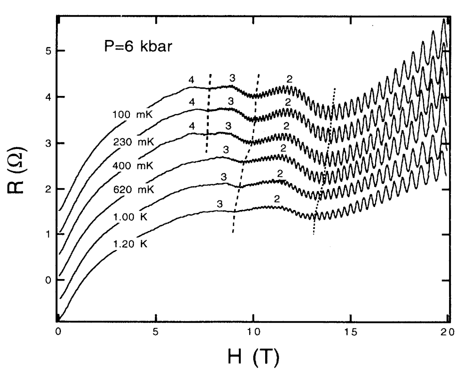

FIG. 2. Magnetoresistance and the SdH effect in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ vs temperature for $P = 6$ kbar. Indices refer to Landau levels associated with the anomalous oscillations. Dashed lines indicate the temperature dependence of the oscillation positions.

have a Landau level index of about 20–60.

In Fig. 3(a), the Landau indices for the slow oscillations vs inverse field are shown for the different pressures at $T \approx 150$ mK. Due to the low quantum numbers observed, we have used half integers (both the maxima and minima) of the SdH oscillations to index the oscillations. The background magnetoresistance was subtracted and the fast oscillations filtered out in order to allow a more precise determination of the extrema of the slow oscillations. The uncertainty in determination of these points is less than the size of the data point markers in Fig. 3(a), except for the high-field points, where the presence of large-amplitude fast oscillations disguises the maximum. The pressure dependence of the SdH frequency for both the hole orbit (from the Fourier transform) and the new oscillations [from the slopes in Fig. 3(a)] are presented in Fig. 3(b). Here we find the pressure dependence to be of opposite sign for the two orbits. We note that the 4 and 6 kbar data are similar; we attribute this to the pressurization history of the sample. The 4 kbar measurement was taken after the higher-pressure data, with the sample depressurized and repressurized. It is possible that trapped pressure effectively increased the low-temperature pressure of the 4 kbar point upwards towards the 6 kbar pressure.

Although the magnitudes of the change in SdH frequencies with pressure shown in Fig. 3(b) for the two types of oscillations are similar in size, there is no simple relationship evident from the calculated band structure given by Mori *et al.*[1] This band structure is depicted in Fig. 4 (E_C and E_O in Fig. 4 refer to the closed- and

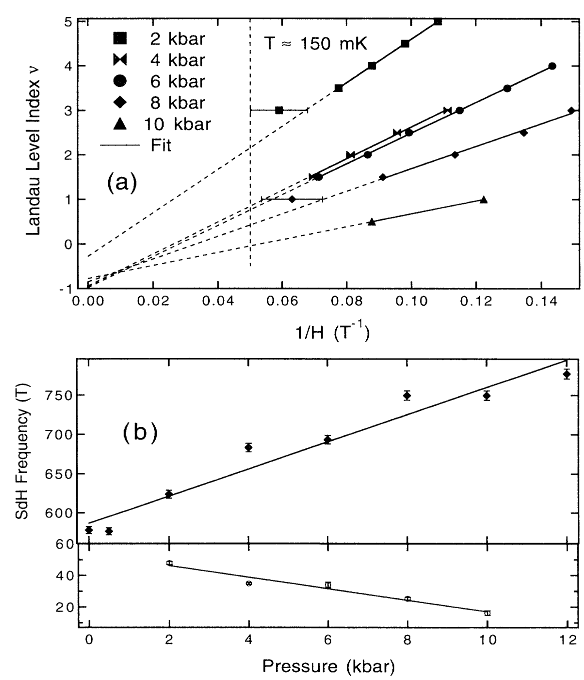

FIG. 3. (a) Landau level index of anomalous oscillations vs $1/H$ for different pressures, at $T = 150$ mK. The vertical line indicates the maximum field of 20 T used in this experiment. (b) Pressure dependence of oscillation frequency for both the hole orbit (top) and the anomalous oscillation orbit (bottom).

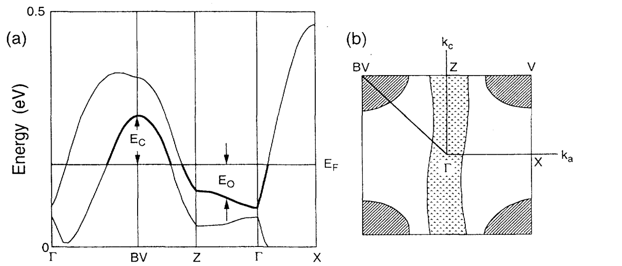

FIG. 4. Band structure and Fermi surface of α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ from Ref. 1. (a) Hole band and open-orbit bands are indicated by darkened lines. Hole and open bandwidths relevant to the discussion in the text are indicated. (b) Closed-orbit (around the BV point) and open-orbit (along the ΓZ line) sections of the Fermi surface.

open-orbit band energies with respect to the Fermi level). To understand the origin of the new oscillation phenomena, we must estimate the effects of pressure on the electronic structure. The compressibility of the related material κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is $K_b=0.025$ (GPa^{-1}), and $K_a \approx K_c = 0.036$ (GPa^{-1}).[12] One effect of pressure is to increase the size of the Brillouin zone, and to "magnify" the topology of the Fermi surface within it. We have estimated this effect from the compressibility data and find that this mechanism could account for about 30% of the observed increase in extremal area with pressure. A second effect is the increase in Fermi level due to a change in carrier density. With the unit-cell parameters $a=1.0091$, $b=2.0595$, and $c=0.9963$ nm, we find that the pressure dependence of the Fermi level is $dE_F/dP = 2/3(K_a+K_b+K_c)E_F(0) \approx 1-10$ meV/kbar, depending on the value of $E_F(0)$. The third effect is the change in the effective mass and in the band energy with pressure. With the assumption of parabolic bands for both the fast and slow oscillation sequences, a change in the effective mass will change the energy dispersion, and, consequently, the Fermi surface area. The increase of bandwidth with increasing pressure will cause the bands to move up or down in energy with respect to the Fermi level, and therefore changes the Fermi surface area. The effective mass of the fast oscillations $m_h=(1.4\pm0.2)m_e$ determined from our SdH measurements shows no pressure dependence within our experimental scatter. This value is lower than other values of m_h obtained from transport data, but close to values measured from cyclotron resonance.[4,13] Singleton *et al.* attribute the difference between the effective mass measured through cyclotron resonance and the (higher) mass gotten from transport data to the effect of electron-electron interaction in the latter case. Perhaps the presence of even small amounts of pressure is sufficient to reduce the strength of electron-electron interactions in this material and decrease the effective mass to that measured in cyclotron resonance. The model that is thus most consistent with our data is that of an increase of E_C and a decrease of E_O with pressure, with little change in dispersion, causing the top of the hole band to move up, and the bottom of the slow oscillation band to rise with respect to the Fermi level. We estimate that the changes in E_C and E_O are 5 meV/kbar and -3 meV/kbar, respectively.

Our results indicate that, unlike in the hole band, the effect of pressure on the slow oscillations arises from a change in the nesting condition of the open orbits, and not directly from the pressure dependence of the bandwidth E_O. The above discussion provides a basis for this assertion. By inspection of the calculated band structure from Ref. 1 in Fig. 4(a), the open orbit band (E_O) is about 45 meV below the Fermi level at the Z point in the Brillouin zone. From our estimates of the pressure dependence of the bandwidths above, the electron band would be at E_F at the Z point at a pressure of at least 15 kbar. Since the slow oscillations appear by 2 kbar, it is unlikely that the open band would have moved upwards with respect to the Fermi level at such low pressure. Furthermore, if pressure did close the open band, this would give an extremal area too large (by a factor of about 10) to describe the slow oscillations. Hence some other mechanism must be responsible for producing closed orbits, and the most plausible explanation is that the slow oscillations result from pressure-induced nesting of the open electron orbits. We know that the nesting must be incomplete at low pressures, since the material has a superconducting, rather than a density-wave, ground state. This partial nesting allows for the formation of closed pockets of carriers associated with the open-orbit portion of the Fermi surface. These pockets need not be large; the slow oscillation frequency at 2 kbar corresponds to an area just 0.5% of the first Brillouin zone. The fact that pressure can change the nesting condition in organic conductors is known to occur in both (Q1D)[14] and (Q2D)[8,15] organic conductors.

We may now describe the behavior of the material with increasing pressure. For $M=NH_4$, deviations from perfect nesting, cased by higher harmonic content in the open-orbit dispersion, allow superconductivity at low temperatures, since no density-wave state occurs. Because of the lack of slow oscillations under ambient pressure at fields above the superconducting critical field, it is clear that the orbits remain unnested in the normal state without pressure. Application of pressure above 2 kbar enhances the nesting condition (i.e., reduces the higher-order dispersion). This allows parts of the open-orbit Fermi surface to nest, thereby producing small closed-orbit pockets which are responsible for the slow oscillation effects. The partial nesting removes some, but not all, of the superconducting density of states which remain on the ungapped pieces of the open-orbit Fermi surface, and this helps to reduce T_c. Further reductions in T_c are most likely caused by the inverse square relationship of the BCS interaction term $\lambda=[N(0)V]$ to the Debye frequency ω_D, which is expected to increase with pressure.[14] Above 4 kbar, our results indicate that the nested area is reduced, and at 14 kbar, there is no nesting of the open orbits. Clearly, because of the sensitivity of the slow oscillations to temperature, pressure, and magnetic field, the deviations from perfect nesting in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ are small in size (of order 1 meV). Their origin most likely arises from the small differences in the size and symmetry of NH_4 from the monometallic cation series K, Rb, and Tl.

What is the difference between α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ and its sister compounds? In all of the other members, where M=K, Rb, or Tl, a density-wave state appears below 8–10 K, which precludes the onset of superconductivity. This state is a result of essentially perfect nesting of the open orbits: there are no slow oscillations observed, and when the nesting is destroyed at high magnetic field, there is a dramatic change in the background magnetoresistance which sets the scale of the degree of nesting. The destruction of nesting at high pressure (above about 10 kbar) is seen in all of the materials we have studied. For M=K,[8,15] this is evidenced by the elimination of the kink field magnetoresistance behavior of this material. The removal of the density-wave state with pressure is also seen in the Rb material;[16] similar behavior is expected for the Tl compound. Based on the pressure dependence of the BCS parameters for T_c, reentrant superconductivity with pressure is unlikely in any member of the family.

Before concluding, it is relevant to discuss briefly the near-quantum limit behavior of the slow oscillations. What is quite unusual is the behavior of the slow oscillations near 15 T. If we assume a parabolic band with the pressure dependence deduced from Fig. 3(b), then the slow oscillation bandwidth at 10 kbar is about 5 meV. Our analysis of the slow oscillations indicates an effective mass $m^* \approx 1.5 m_e$, and a Dingle temperature of 2–3 K. Hence, from Fig. 3(a), the spacing of the Landau levels is about 1 meV at 15 T. From Figs. 2 and 3, it is evident that the ν=1 Landau level is shifted to higher fields, and does not follow the $1/H$ progression. An estimate of the Landau level broadening based on the slow oscillation Dingle temperature gives a Γ of 0.2 meV. Hence it is possible that the broadening leads to the deviations from $1/H$ dependence when the system reaches the near-quantum limit condition. Another possibility is that the nesting condition is sensitive to pressure related parameters such as thermal expansion and magnetorestrictive effects. Sensitivity to thermal expansion would explain the temperature dependence seen in Fig. 2; the absence of lower Landau level indices in the lower-pressure data supports the idea that magnetorestrictive effects disturb the delicate conditions necessary for partial nesting of the open-orbit FS.

We conclude that the difference in symmetry or mass of the NH$_4$ member of the otherwise monatomic M cation series in α-(BEDT-TTF)$_2M$Hg(SCN)$_4$ leads to imperfect nesting of the open electron orbits. This allows superconductivity at low temperatures and ambient pressure in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$. Pressure destroys superconductivity in α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ by reducing the BCS parameter $N(0)V$, and enhances the nesting condition. The pressure-induced nesting produces closed orbits which give rise to the slow oscillations. At higher pressures, the nesting is monotonically reduced. In the monatomic cation series, the nesting is perfect at low temperatures, but the nesting condition is destroyed at high pressure and/or magnetic field. Our results show that under special conditions the near-quantum limit can be reached in the quasi-two-dimensional organic systems. Refined band structure and theoretical work is needed to work out the details of the nesting condition and its pressure and field dependence in this series of materials.

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