Pressure-induced nesting in the low-dimensional organic superconductor 
\( \alpha-(\text{BEDT-TTF})_2\text{NH}_4\text{Hg(SCN)}_4 \)

S. J. Klepper
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

J. S. Brooks*
Clark University, Worcester, Massachusetts 01610

X. Chen
Department of Physics, Boston University, Boston, Massachusetts 02215

I. Bradaric
Vinca Institute—Laboratory for New Industrial Materials, 11001 Belgrade, Yugoslavia

M. Tokumoto, N. Kinoshita, and Y. Tanaka
Electrotechnical Laboratory, Tsukuba, Ibaraki 305, Japan

C. C. Agosta
Clark University, Worcester, Massachusetts 01610

(Received 19 July 1993)

Why superconductivity appears in only one member (M = NH₄) of the isostructural family of organic conductors \( \alpha-(\text{BEDT-TTF})_2\text{MHg(SCN)}_4 \) 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 \( \alpha-(\text{BEDT-TTF})_2\text{NH}_4\text{Hg(SCN)}_4 \) at 1.0 K. Our results show a remarkable pressure dependence of the Fermi surface topology. We argue that with NH₄ there are small deviations from perfect nesting of the open-orbit bands which favor superconductivity over a density-wave state.

\( \alpha-(\text{BEDT-TTF})_2\text{MHg(SCN)}_4 \), where (BEDT-TTF) is bis(ethylenedithio)tetrathiafulvalene, is a family of quasi-two-dimensional (Q2D) organic conductors (where M = NH₄, K, Tl, or Rb)\(^{1,2} \) of great interest due to their low-temperature properties, which include superconductivity for M = NH₄ (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 \( \alpha-(\text{BEDT-TTF})_2\text{NH}_4\text{Hg(SCN)}_4 \) exhibits a single Shubnikov–de Haas (SdH) frequency of 568 T in high magnetic fields.\(^4 \) In contrast, \( \alpha-(\text{BEDT-TTF})_2\text{KHg(SCN)}_4 \), \( \alpha-(\text{BEDT-TTF})_2\text{RbHg(SCN)}_4 \), and \( \alpha-(\text{BEDT-TTF})_2\text{TlHg(SCN)}_4 \) 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\(^5 \) and the behavior of the background and oscillatory magnetoresistance\(^6,9 \) to the influence of the open orbits. The motivation for this work was to remove the superconductivity in \( \alpha-(\text{BEDT-TTF})_2\text{NH}_4\text{Hg(SCN)}_4 \) 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 \( dT_c/dP = -0.25 \) 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 \( \alpha-(\text{BEDT-TTF})_2\text{NH}_4\text{Hg(SCN)}_4 \) induced by pressure has magnetoresistance 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 anom-
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 indicate some peaks of the anomalous slow oscillations.

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
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 \( \alpha\text{-}(\text{BEDT-TTF})_2\text{MgHg(SCN)}_4 \) 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 \( \Gamma Z \) line) sections of the Fermi surface.

We may now describe the behavior of the material with increasing pressure. For \( M = \text{NH}_4 \), deviations from perfect nesting, caused 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 low oscillations under ambient pressure at fields above the superconducting critical field, it is clear that the orbits remain unnestled 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 \( T^* \). Further reductions in \( T^* \) are most likely caused by the inverse square relationship of the BCS interaction term \( \lambda = [N(0)V]^{-1} \) to the Debye frequency \( \omega_D \), which is expected to increase with pressure. 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 \( \alpha\text{-}(\text{BEDT-TTF})_2\text{NH}_4\text{Hg(SCN)}_4 \) are small in size (of order 1 meV). Their origin most likely arises from the small differences in the size and symmetry of \( \text{NH}_4 \) from the monometallic cation series \( K \), \( \text{Rb} \), and \( \text{Tl} \).
What is the difference between $\alpha$-(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, 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; 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. This suggests a kink in the high-field magnetoresistance behavior of this material. The removal of the density-wave state with pressure is seen in the Rb material; a 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.

Research at Boston University was supported by NSF Grant No. DMR 92-14889. The authors are indebted to the staff of the Francis Bitter National Magnet Laboratory (supported by the National Science Foundation) where this work was carried out.