

Shubnikov–de Haas effect in the organic superconductor κ -(BEDT–TTF)₂Cu[N(CN)₂]Cl under pressure

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The interplane magnetoresistance of a layered organic superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]X with X=Cl is studied under pressure from 2 to 10 kbar. Shubnikov–de Haas oscillations are found above 8 T, in the whole pressure range. The oscillation behavior is remarkably different from that observed in the isostructural Br-containing analog. On the other hand, it resembles the features found previously in the κ -(BEDT-TTF)₂Cu(NCS)₂ superconductor. © 1995 American Institute of Physics.

Isostructural quasi-two-dimensional organic superconductors κ -(BEDT-TTF)₂X with polymeric anions X=Cu[N(CN)₂]Br and Cu[N(CN)₂]Cl (hereafter referred to as Br and Cl salts, respectively) have been of special interest for the last five years primarily because of their superconducting critical temperatures ≈ 12 – 13 K, the highest among the charge-transfer organic metals.¹ In order to understand the mechanism of superconductivity in these compounds, detailed information about their conducting system is highly desirable. During the past few years, a number of attempts to find quantum magnetic oscillations have been made by several groups. Only very recently, Shubnikov–de Haas (SdH) oscillations of a low amplitude were found in the Br salt under a pressure of ≈ 9 kbar (Ref. 2), providing a direct evidence for the Fermi-liquid character of its electronic system. The oscillation parameters have revealed a significant difference between the Fermi surfaces (FS) of the Br salt and of a similar compound, κ -(BEDT-TTF)₂Cu(NCS)₂, in contradiction with the theoretical predictions.¹

To understand this difference, more-detailed study of the κ -type family is necessary. In particular, a search for SdH oscillations in the Cl-salt, which is the nearest isostructural analog of the Br-salt, should be very informative. In this Letter, we report the first observation of the SdH effect in κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl and compare the results with those previously obtained on the Cu(NCS)₂- and Br-containing compounds.

The crystal used in this work was grown electrochemically and had the shape of a

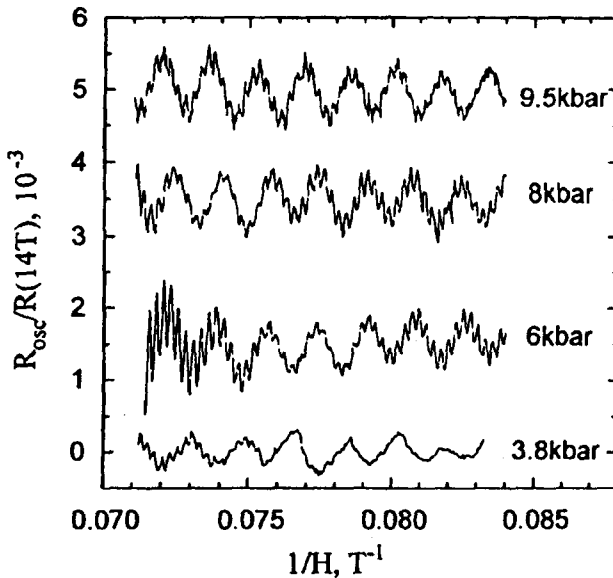


FIG. 1. Normalized oscillatory part of the interplane resistance of κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl versus the inverse magnetic field at different pressures at 1.4 K. The magnetic field is applied normal to the *ac* plane.

distorted hexagon with dimensions of $\sim 0.8 \times 0.2 \times 0.5$ mm. The interplane (i.e., normal to the highly conducting *ac* plane of the crystal) resistance was measured at temperatures 1.4–4.2 K in magnetic fields up to 14 T directed normal to the *ac* plane. Since the Cl salt is known to be a magnetic semiconductor at low temperatures at ambient pressure, all the measurements were done under quasi-hydrostatic pressure in the range of 2 to 9.7 kbar, using a Cu–Be clamp pressure cell with a silicone oil as a pressure medium. The pressure up to 12 kbar was applied at room temperature and corrected for the low temperatures in the same way as in Ref. 2.

The interplane resistance of the sample at room temperature was found to decrease by a factor of 13 on loading from 0 to 12 kbar; no special features which could be ascribed to a phase transition were detected, in agreement with Ref. 3. Within the whole pressure range, the compound exhibits a metallic behavior, its resistance decreasing upon cooling of the sample. Although the superconducting transition is suppressed with increasing pressure, small signs of superconducting fluctuations survive up to the highest pressure applied. The magnetoresistance $\Delta R(H) = R(H) - R(0)$ grows to $\approx 0.15R(0)$ at $H = 10$ T and starts to decrease slowly at higher fields. The details of the monotonic magnetoresistance will be presented in a forthcoming paper.⁴

SdH oscillations were detected at $T = 1.4$ K and in fields above 8 T. Figure 1 shows the oscillatory part of the resistance, normalized to its background value at 14 T, for several different pressures. Prominent oscillations of two frequencies can be readily distinguished, as can be seen in Fig. 2 for $P = 6$ kbar. The frequencies $F_\alpha(6 \text{ kbar}) = 577$ T and $F_\beta(6 \text{ kbar}) = 3880$ T correspond to FS cross sections of $5.52 \times 10^{14} \text{ cm}^{-1}$ and $3.72 \times 10^{15} \text{ cm}^{-1}$, respectively. Using the room temperature crystallographic parameters³

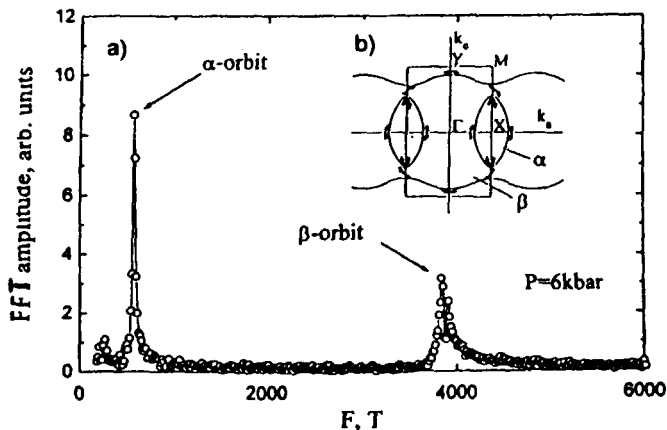


FIG. 2. Fast Fourier transformation spectrum of the SdH oscillations at $P=6$ kbar; inset: FS cross section in the 2D plane³ and the orbits responsible for the SdH oscillations.

and extrapolating them to low temperatures according to the ambient-pressure thermal contraction data,⁵ we estimate $S_{\alpha}=(0.147\pm 0.002)S_{BZ}$ and $S_{\beta}=(0.99\pm 0.005)S_{BZ}$, where S_{BZ} is the cross-sectional area of the first Brillouin zone in the 2D plane. The cyclotron masses extracted from the temperature dependences of the oscillation amplitudes are: $\mu_{\alpha}\equiv m_{\alpha}/m_0=1.7\pm 0.05$ and $\mu_{\beta}=3.5\pm 0.1$.

The inset in Fig. 2 shows the α and β orbits corresponding to the observed oscillations, on the FS drawn with allowance for the band-structure calculations.³ The α oscillations are associated with the classical orbits on the hole-like cylinder positioned near the Brillouin zone boundary XM . The β oscillations originate from a magnetic breakdown which gives rise to new closed orbits, including both the open electron-like sheets and the outer arcs of the hole-like cylinders, with an area equal to the whole Brillouin zone area. The calculations³ predict a 2-fold degeneracy of the FS at XM due to the presence of the center of inversion symmetry in the crystal structure. In this case, one should expect only the F_{β} frequency in the oscillation spectrum (as if in the case of complete magnetic breakdown). However, we observe, prominent α oscillations. This indicates that a gap really exists in the Cl salt. This discrepancy might be explained by the spin-orbit interaction, which was not taken into account in the calculation.³ On the other hand, one could propose that pressure lowers the crystal symmetry, thus removing the degeneracy.

The data obtained here closely resemble those found for the $\text{Cu}(\text{NCS})_2$ salt.^{7,8} In the latter compound, the FS has been shown to be very similar to that shown in Fig. 2, consisting of a cylinder and a pair of warped open sheets separated from the cylinder by a small energy gap at the Brillouin zone boundary. The only significant difference is that the gap between the hole-like and electron-like parts of the FS is larger due to the lack of inversion symmetry in the monoclinic structure of the $\text{Cu}(\text{NCS})_2$ salt.⁷ This is reflected in a remarkably higher contribution of the α oscillations below 15 T in this compound.

As is seen in Fig. 1, the oscillations at both frequencies exist in the whole pressure range, their amplitude varying only slightly with changing pressure. Figure 3 shows the

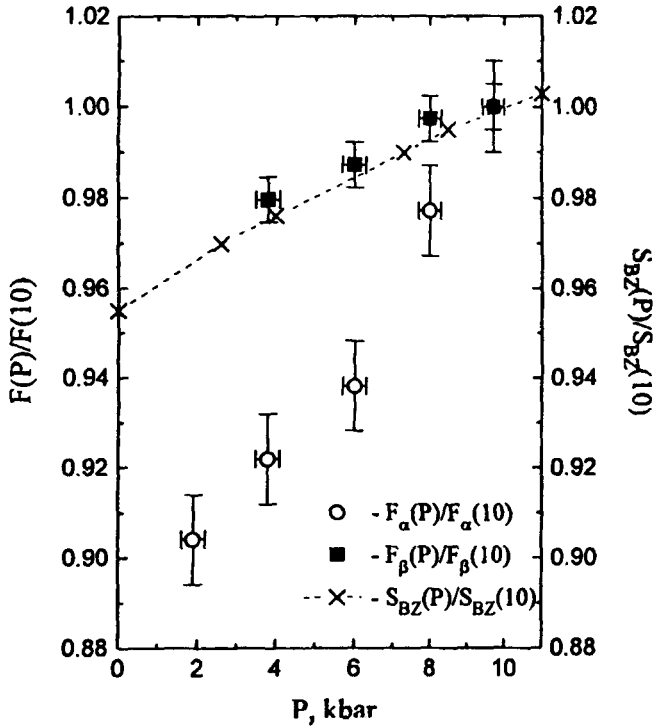


FIG. 3. Pressure dependence of frequencies F_α and F_β normalized to their values at 10 kbar. Crosses represent the pressure dependence of the Brillouin zone cross-sectional area taken from Ref. 3: ○— $F_\alpha(P)/F_\alpha(10)$, ■— $F_\beta(P)/F_\beta(10)$, ×— $S_{BZ}(P)/S_{BZ}(10)$.

experimentally obtained pressure dependences of F_α and F_β along with that of the Brillouin zone area estimated from Ref. 3. Again, the behavior resembles that of the $\text{Cu}(\text{NCS})_2$ salt,⁶ with $F_\beta(P)$ strictly following the pressure dependence of the crystal parameters and with a much sharper slope of $F_\alpha(P)$.

Thus the results prove that the FS of the Cl and $\text{Cu}(\text{NCS})_2$ salts are very similar to each other. At the same time, the SdH oscillations in the Br-containing analog show the following remarkably different features: i) the oscillations arise only above a threshold pressure of ~ 8 kbar (Ref. 2); ii) the frequency of the α oscillations, 155 T, is a factor of 4 smaller than in the case of the Cl and $\text{Cu}(\text{NCS})_2$ salts;² iii) despite the predicted absence of an energy gap between the hole-like and electron-like parts of the FS, the β oscillations have been detected only above 24 T, and they remain much smaller than the α oscillations up to $H = 30$ T (Ref. 4). At the moment, the reasons for these striking differences are not understood. Judging from a comparison of the crystal structures of all three compounds, one would expect the FS of the Cl salt to be much more similar to that of the Br-containing analog than to the $\text{Cu}(\text{NCS})_2$ salt. One could suppose that the extended Hückel model band-structure calculations give a wrong result for the Br salt and that its FS is entirely different at room temperature. This would be surprising, however, since the

model is fundamentally valid for the other two salts. Another possible reason might be a pressure-induced phase transition in the Br salt, as mentioned in Ref. 2.

Further comprehensive studies of the κ -type family are necessary in order to solve this problem. One clue may lie in an investigation of the mixed compounds κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl_{1-x}Br_x ($0 < x < 1$) that is planned for the near future.

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