

SHUBNIKOV-de HAAS EFFECT IN THE ORGANIC SUPERCONDUCTOR κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl UNDER PRESSURE

M.V.Kartsovnik^{†*}, W.Biberacher^{*}, K.Andres^{*}, N.D.Kushch[□]

[†] Institute of Solid State Physics RAS
142432 Chernogolovka, Moscow distr., Russia

^{*} Walther-Meissner-Institut
D-85748 Garching, Germany

[□] Institute of Chemical Physics RAS
142432 Chernogolovka, Moscow distr., Russia

Submitted 16 November 1995

The interplane magnetoresistance of a layered organic superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]X with X = Cl has been studied under pressure from 2 to 10 kbar. Shubnikov-de Haas oscillations have been 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.

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 due to their superconducting critical temperatures $\approx 12 - 13$ K, the highest among the charge-transfer organic metals [1]. In order to understand the mechanism of superconductivity in these compounds, the 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 pressure of ≈ 9 kbar [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 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, the search of the SdH oscillations in the Cl-salt, which is the nearest isostructural analog of the Br-salt, must 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-compounds.

The crystal used in this work was grown electrochemically and had the shape of a distorted hexagon with dimensions of $\sim 0.8 \times 0.2 \times 0.5$ mm³. The interplane (i.e. normal to the crystal highly-conducting *ac*-plane) 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 silicon 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 [2].

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

At $T = 1.4$ K and fields above 8 T, SdH oscillations have been detected. Fig.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 shown 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 the 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 parameters [3] 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 area of the first Brillouin zone cross-section 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 $\mu_\beta = 3.5 \pm 0.1$.

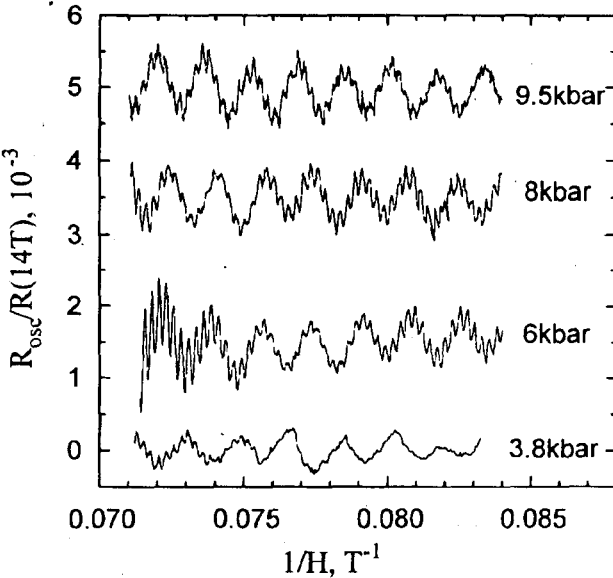


Fig.1. Normalized oscillatory part of the interplane resistance of $\kappa\text{-(BEDT-TTF)}_2\text{Cu[N(CN)}_2\text{)]Cl}$ vs. inverse magnetic field at different pressures at 1.4 K. The magnetic field is applied normal to the ac -plane

Inset in Fig.2 shows the α - and β -orbits, corresponding to the observed oscillations, on the FS drawn with the account of 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

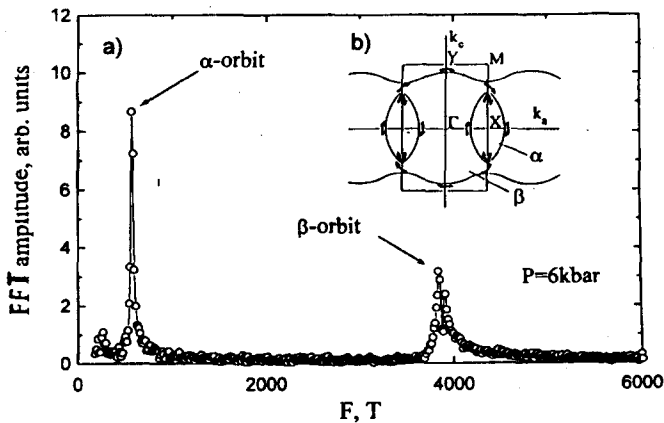


Fig.2. Fast Fourier transformation spectrum of the SdH oscillations at $P=6$ kbar; inset: FS cross-section in the 2D plane [3] and the orbits responsible for the SdH oscillations

open electron-like sheets and the outer arcs of the hole-like cylinders, with the area equal to the whole Brillouin zone area. The calculations [3] predict a 2-fold degeneracy of the FS at XM due to the presence of the inversion symmetry center 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). We observe, however, prominent α -oscillations. This indicates that the gap really exists in the Cl-salt. This discrepancy might be explained by 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 obtained data closely resemble those found for the $\text{Cu}(\text{NCS})_2$ -salt [7, 8]. In the latter compound, the FS is established 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 consists in that the gap between the hole- and electron-like parts of the FS is larger due to the lack of the 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 of both frequencies exist in the whole pressure range, their amplitude varying only slightly with changing pressure. Fig.3 shows the experimentally obtained pressure dependences of F_α and F_β along with that of the Brillouin zone area estimated from [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 a much sharper slope of the $F_\alpha(P)$.

Thus, the obtained 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 [2]; ii) the frequency of the α -oscillations, 155 T, is a factor of 4 smaller than in the case of Cl- and $\text{Cu}(\text{NCS})_2$ -salts [2]; iii) despite the predicted absence of the energy gap between the hole- and electron-like FS parts, the β -oscillations have been detected only above 24 T, still they remain much smaller than the α -oscillations up to $H=30$ T [4]. At the moment, the reasons for these striking differences are not understood. Basing on the comparison between the crystal structures of all the three compounds, one would expect the FS of the Cl-salt to be much more

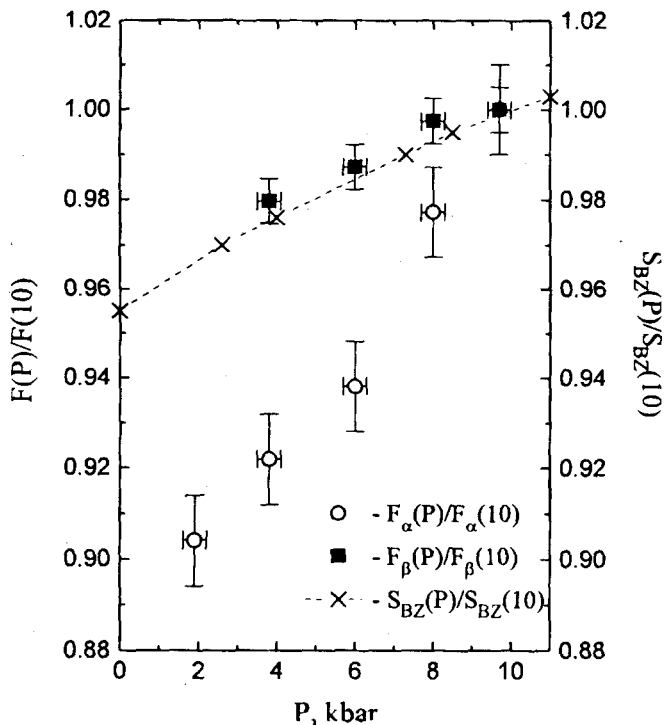


Fig.3. Pressure dependence of frequencies F_{α} and F_{β} normalized to their values at 10 kbar. Crosses represent the pressure dependence of the Brillouin zone cross-section area taken from [3]: $\circ - F_{\alpha}(P)/F_{\alpha}(10)$, $\blacksquare - F_{\beta}(P)/F_{\beta}(10)$, $\times - S_{BZ}(P)/S_{BZ}(10)$

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 its FS is entirely different at room temperature. This would be surprising, however, since the model is principally valid for the other two salts. Another possible reason might be a pressure-induced phase transition in the Br-salt, as mentioned in [2].

Further comprehensive studies of the κ -type family is necessary to solve this problem. One of the clues may lie in the investigation of the mixed compounds, $\kappa\text{-(BEDT-TTF)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}_{1-x}\text{Br}_x$ ($0 < x < 1$), that is planned to do in near future.

The work was supported by the NATO Laboratory Linkage program, grant HTECH.LG 930278. One of the authors (M.V.K) also acknowledges partial support by the Russian Foundation for Fundamental Research, grant 93-02-14246 and International Science Foundation, grant RES300.

1. J.M.Williams, J.R.Ferraro, R.J.Thorn et al., *Organic Superconductors: Synthesis, Structure and Theory*, Prentice Hall, New Jersey, 1992.
2. M.V.Kartsovnik, G.Yu.Logvenov, H.Ito et al., *Phys. Rev. B* **52**, (1995) in press.
3. A.J.Schultz, H.H. Wang, J.M.Williams et al., *Physica C* **234**, 300 (1994).
4. M.V.Kartsovnik, W.Biberacher, K.Andres et al., to be published.
5. M.Kund, K.Andres, H.Müller, and G.Saito, *Physica B* **203**, 129 (1994).
6. J.Caulfield, W.Lubczynski, F.L.Pratt et al., *J. Phys.: Condensed. Matter* **6** 2911 (1994).
7. K.Oshima, T.Mori, H.Inokuchi et al., *Phys. Rev. B* **38**, 938 (1988).
8. T.Sasaki, H. Sato, and N. Toyota, *Solid State Commun.* **76**, 507 (1990); C.-P. Heidmann, H. Müller, W. Biberacher et al., *Synth. Metals* **41-43**, 2029 (1991).