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MAGNETIC QUANTUM OSCILLATIONS IN THE ORGANIC SUPERCONDUCTOR κ-(BEDT-TTF)$_2$CU[N(CN)$_2$]BR

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The interlayer magnetoresistance of the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br has been measured at ambient pressure and under pressure up to 12.5 kbar. In addition to the slow Shubnikov-de Haas oscillations with the frequency $\simeq$ 150 T observed at $P \geq 5$ kbar, rapid oscillations attributed to the magnetic breakdown orbit enveloping the area equal to 100% of the Brillouin zone area are found to emerge above $B = 20$ T. The latter oscillations are observed at ambient pressure as well as under pressure up to 9 kbar.

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The organic salts κ-(BEDT-TTF)$_2$X where BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene and X = Cu(NCS)$_2$, Cu[N(CN)$_2$]Cl$_{1-x}$Br$_x$ ($0 \leq x \leq 1$), and Cu(CN)[N(CN)$_2$] are characterized by a layered crystal structure with the BEDT-TTF molecules arranged in mutually orthogonal dimers and forming conducting layers alternating with insulating layers of the anions X [1, 2]. These compounds have been of high interest for the last years due to the wide range of physical properties which they exhibit in spite of very similar crystal structures. For example, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is a metal at low temperatures and undergoes a superconducting transition at 9.4 K [3]. At the same time, the salt with X = Cu[N(CN)$_2$]Cl undergoes a metal-to-insulator transition into an antiferromagnetically ordered state which is supposed to be of the Mott type [4]. A moderate pressure (≥ 0.3 kbar) stabilizes the metallic state and the compound becomes a superconductor with $T_c = 12.8$ K, the highest among the known organic superconductors [1]. Its close isostructural analog, the salt with X = Cu[N(CN)$_2$]Br can be regarded as one located nearest to the boundary between the metallic and insulating states: The salt containing hydrogen in the BEDT-TTF molecules, κ-(h_8,BEDT-TTF)$_2$Cu[N(CN)$_2$]Br exhibits a metal-like behaviour at low temperatures, although with highly pronounced electron correlations (see *e.g.* [5]), and undergoes the superconducting transition at $T_c = 11.2$ K [1], whereas the deuterated salt, κ-(d_8,BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, is suggested to have a charge gap at the Fermi level [6].

The effect of subtle changes introduced by the substitution of different anions on the electronic groundstate of the κ-type salts is not understood so far. The band structure calculations made conventionally in the two-dimensional approximation (i.e. assuming that the electronic bands are formed by only the BEDT-TTF layers) give

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very similar results for all the three compounds [1, 7, 8]. These results have been thoroughly proved by numereous studies of the magnetic quantum oscillations in the Cu(NCS)$_2$ salt (see *e.g.* [7, 9]). Recent observations of the Shubnikov-de Haas effect in the metallic state (under pressure) of the κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl [10] confirm the predicted Fermi surface for this compound. However, neither quantum oscillations nor classical galvanomagnetic effects which could be directly related to the Fermi surface shape have been found in the Cu[N(CN)$_2$]Br salt at ambient pressure till now. Very weak Shubnikov-de Haas oscillations have been observed in this compound at pressure $P \approx 9$ kbar [11, 12]. The oscillation parameters [11] revealed considerable differences in the Fermi surface with respect to the Fermi surfaces of the Cu(NCS)$_2$ and Cu[N(CN)$_2$]Cl salts, in contradiction with the theoretical predictions. In particular, the frequency of the slow oscillations which could be attributed to the classical hole orbit at the cylindrical part of the Fermi surface was found to be a factor of 4 smaller than in the other two compounds. This result suggests that either the Fermi surface of the Cu[N(CN)$_2$]Br salt strongly deviates from the predicted one [1] already at ambient pressure or it is unusually sensitive to the applied pressure.

In order to get further information about the Fermi surface of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and its pressure dependence, we have carried out high-field magnetoresistance measurements on this compound. In this paper we present the quantum magnetoresistance oscillations of two different frequencies which are attributed to the Fermi surface cross-sections constituting 100% and $\approx 4\%$ of the corresponding Brillouin zone cross-section area, respectively. The higher frequency oscillations are found down to $P = 0$ kbar, thus providing the first direct evidence for the well defined Fermi surface existing at ambient pressure.

The high quality crystal of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br used for the experiment was grown electrochemically as described elsewhere [13]. The interlayer (i.e. perpendicular to the crystal highly conducting ac-plane) resistance was measured down to $T = 0.4$ K by means of the standard a.c.-method with an excitation current of 10 to 100 μA. The contact resistance was less than 10 Ω while the sample resistance varied from ~ 3 to 35 Ω depending on the pressure applied. A BeCu clamp cell was used to generate the quasi-hydrostatic pressure up to 15 kbar at the room temperature that corresponded to ≈ 12.5 kbar at low temperatures. The magnetic field up to 27 T perpendicular to the ac-plane was provided by the hybrid magnet at the High Magnetic Field Laboratory, MPI-CNRS, Grenoble.

The main panel of Fig.1 represents the high-field trace of the magnetoresistance at ambient pressure at $T = 0.41$ K. Clear oscillations with the frequency of 3790 ± 30 T (see the fast Fourier transformation in the inset a) of Fig.1) indicate the electron orbit in the k-space with the area equal to 100% of the Brillouin zone cross-section area as calculated from the room temperature crystal parameters [1] taking into account the thermal contraction [14]. This is the first observation of the magnetic quantum oscillations in the present compound at ambient pressure. The cyclotron mass estimated from the temperature dependence of the oscillation amplitude is $(6.4 \pm 0.5)m_e$ where m_e is the free electron mass. Thus the oscillations are similar to the magnetic breakdown oscillations found earlier in the other κ-salts, with X = Cu(NCS)$_2$ and Cu[N(CN)$_2$]Cl [9, 10].

Fig.2 shows the oscillatory magnetoresistance normalized to the background resistance at several pressures. Oscillations of two main frequencies, $F_\alpha \simeq 150$ T and $F_\beta \simeq 3900$ T (hereafter referred to as α- and β-oscillations), can be generally resolved, in agreement with the previous observation at $P \approx 9$ kbar [12]. The

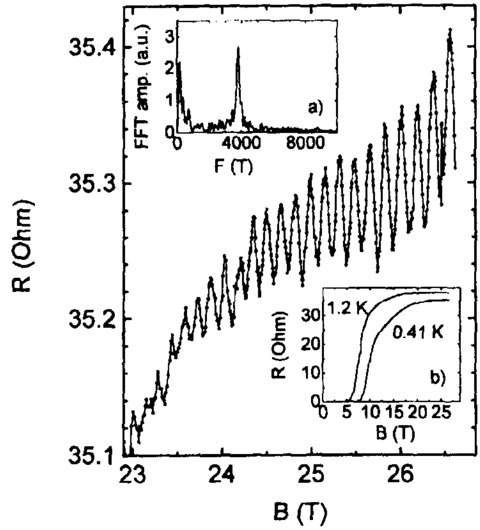

Fig.1. High magnetic field fragment of the interlayer magnetoresistance at ambient pressure, $T = 0.41$ K. Inset a) - fast Fourier spectrum of the oscillations. Inset b) - field dependencies of the interlayer resistance at $T = 0.41$ and 1.2 K

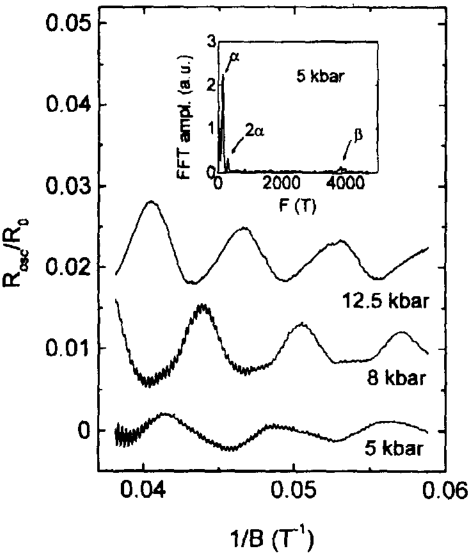

Fig.2. Oscillatory part of the magnetoresistance normalized to the resistance background at different pressures. The curves at 8 and 12.5 kbar are offset for clarity. Inset: fast Fourier spectrum of the oscillations.

β-oscillations correspond to those found at ambient pressure. Their amplitude gradually goes down with increasing the pressure, vanishing above 10 kbar. The oscillation frequency changes with the rate $d\ln F_\beta/dP \approx 3.8 \cdot 10^{-3}$ kbar^{-1}. This rate is similar to the values obtained for the β-oscillations in the salts with X = $Cu(NCS)_2$ [15] and $Cu[N(CN)_2]Cl$ [10]. Since the β-frequency is assumed to directly measure the Brillouin zone cross-section area, its pressure dependence is expected to follow the crystal lattice compressibility. Indeed, the obtained value agrees with the compressibility reported for the κ-salts [8, 16].

The α-oscillations correspond to the Fermi surface extremal cross-section occupying $\approx$ 4% of the Brillouin zone area. Their amplitude is somewhat higher than that reported in [11] and amounts to 1% of the background resistance at around 25 T. The relatively high oscillation amplitude as well as the resistance ratio, $R(293\text{K})/R_N(1.5\text{K}) \approx 50$ and 30 at ambient pressure and under 12.5 kbar, respectively (R_N denotes the normal state resistance extrapolated from the non-superconducting region for $P = 0$ kbar) reflects the good quality of the sample. At increasing the pressure from 5 to 12.5 kbar the frequency F_α gradually grows up from 143 to 163 T. As for the oscillation amplitude, it remains nearly unchanged between 8 and 12.5 kbar but becomes significantly smaller at 5 kbar. No α-oscillations have been observed at ambient pressure within the studied magnetic field range.

Turning to the interpretation of the experimental results, we remind that, like in the other κ-salts, the Fermi surface of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ predicted by the band structure calculations [1] is a linear network extended along the k_a direction and formed by intercoupled cylinders with their axes parallel to the

k_b direction(i.e. perpendicular to the crystallographic ac-plane) and cross-section areas equal to that of the Brillouin zone area. Due to the inversion symmetry characteristic of the crystal structure the lattice potential is expected to give no gap at the points of the intersections between the adjacent cylinders at the Brillouin zone boundary. The observation of only the β-oscillations at ambient pressure seems to be consistent with these predictions. Indeed, if the energy gap at the Brillouin zone boundary is negligibly small, only the orbit over the entire Fermi surface cylinder with the area equal to the Brillouin zone cross-section should contribute to the oscillations. Such case of the nearly complete magnetic breakdown has been found in the isostructural compound κ-(BEDT-TTF)$_2$I$_3$ [17]. The relatively small amplitude of the oscillations in comparison with the latter compound may be attributed to the higher Dingle temperature (it is estimated to be 2.5 ± 0.5 K in the present compound against $T_D < 1$ K in the other κ-salts) and stronger warping of the Fermi surface cylinder. The decrease of the amplitude of the β-oscillations under pressure and simulteneous enhancement of the α-oscillations can be likely explained by structural changes inducing the gap at the Brillouin zone boundary.

As it was noted earlier [11], the α-oscillations reveal a considerable deviation of the Fermi surface from that predicted theoretically, their frequency being a factor of 4 and cyclotron mass a factor of 2 smaller than the expected values. The oscillation parameters obtained in our experiment have not shown any sharp transition or unusually strong changes under pressure. Hence we suggest that the specific features characteristic of the Fermi surface at high pressures remain essentially the same at ambient pressure. A possible explanation of the observed discrepancy may consist in structural changes which have been reported by Nogami et al. [18]. The superlattice reflections found in [18] correspond to doubling of the high temperature lattice along the c direction that should reduce the original Brillouin zone along the k_c-axis and considerably reconstruct the possible electron orbits. In particular, smaller orbits at the folded hole cylinders are likely to be formed. The new orbits may give rise to the slow α-oscillations. Besides, other closed orbits resulting from multiple intersections of the initial Fermi surface cylinder may be expected. They could give different contributions to the oscillation spectrum depending on the interband gaps and magnetic field strength. In this connection, the prominent peak at $F \approx 2F_\alpha$ (see inset in Fig.2) might come from an independent orbit rather than be an anomalously strong second harmonic of the fundamental α-frequency. Obviously, if the interband gaps are very small (that could be if the inversion symmetry survives during the structural transition), the main contribution to the oscillatory resistance should come from the β-orbit enveloping 100% of the Brillouin zone area. This is probably the case we find at $P = 0$ kbar.

We note that the behaviour of the oscillations at low pressures may be considerably affected by the superconduting transition. As it is seen from the field dependencies of the resistance presented in the inset b) of the Fig.1, signs of the superconductivity survive up to fields of $\simeq 20$ T at ambient pressure. This is even more clearly illustrated by Fig.3 in which high-field tracks of the resistance normalized to its values at 27 T are shown for different pressures. For the pressure $P > 0$ kbar the resistance shows almost linear field dependence with the slope increasing with increasing pressure. At the same time the 0 kbar curve shows a very steep initial slope and saturates to the normal behaviour at fields not lower than 23 T. A more detailed study is necessary in order to clarify whether

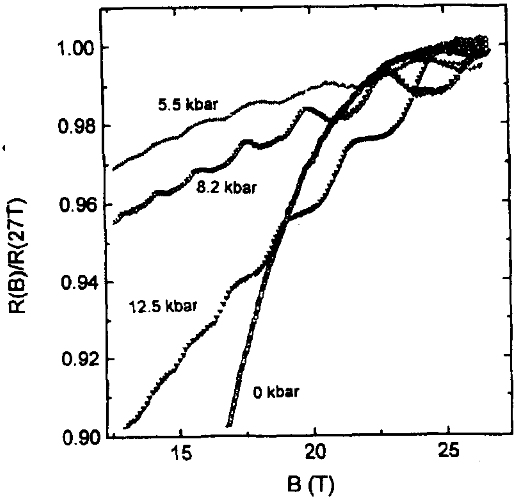

Fig.3. Magnetoresistance above 13 T at different pressures.

it is bulk superconductivity or the fluctuations of the order parameter amplitude which determine the resistance above 10 T but both these factors should obviously strongly suppress the Shubnikov-de Haas effect [19]. Of course, the slow oscillations which normally start to be visible from 10-12 T are much more affected by the superconductivity than the β-oscilaltions arising in fields above 22 T. In principle, this may be another reason why the α-oscillations are not observed at ambient pressure in the studied field range.

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