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Shubnikov–de Haas oscillations in the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene

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Magnetoresistance of the layered organic superconductor κ-(BEDT-TTF)$_2X$ with X=Cu[N(CN)$_2$]Br has been studied under pressure up to $\approx$9 kbar. Prominent oscillations attributed to the Shubnikov–de Haas effect have been found at the highest pressure. The oscillation frequency corresponds to a Fermi-surface cylinder with its axis normal to the crystal highly conducting plane and cross section of 1.56×10^{14} cm^{-2}. The latter value is a factor of 4 smaller than that predicted by band-structure calculations for the ambient pressure.

The organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br belongs to a family of charge-transfer salts based on the electron-donor molecule, bis(ethylenedithio)-tetrathiafulvalene or BEDT-TTF. These salts are characterized by a layered crystal structure in which highly conducting BEDT-TTF cation layers are alternated by "insulating" anions and, consequently, demonstrate highly anisotropic electronic properties.[1] The Fermi surfaces (FS) of these materials are mainly characterized by a slightly warped cylinder with its axis normal to the molecular layers. Many of the BEDT-TTF salts exhibit the Shubnikov–de Haas (SdH) oscillations with the amplitude strongly enhanced due to their high two dimensionality (see for a review Ref. 2).

The compounds κ-(BEDT-TTF)$_2X$, where X =Cu(NCS)$_2$, Cu[N(CN)$_2$]Br, and Cu[N(CN)$_2$]Cl have been of special interest primarily because of their superconducting critical temperatures $\geqslant$ 10 K, the highest among the organic superconductors. Besides, their nonsuperconducting properties have been attracting considerable attention during the past years. The Cu(NCS)$_2$ salt has been subjected to extensive magnetic-field studies, revealing various kinds of magnetic oscillations. This includes the conventional SdH effect on closed FS orbits,[3] magnetic breakdown,[4] and quantum interference oscillations,[5] as well as semiclassical angle-dependent magnetoresistance oscillations.[6] All these phenomena accord with a rather simple extended Hückel model band calculations made in the two-dimensional (2D) approximation[3] and prove the principal validity of the conventional metal theory for this compound. In contrast, neither quantum nor semiclassical magnetoresistance (MR) oscillations have been found so far in the Cu[N(CN)$_2$]Br salt at the ambient pressure despite the close similarity of the predicted electronic band structures.[7] One of the reasons for that might be a much lower quality of the Cu[N(CN)$_2$]Br crystals. This is unlikely, however, since the critical temperature and the width of the superconducting transition, which are commonly sensitive to the defect concentration in organic superconductors, point basically to a good quality of the samples. Other reasons for the lack of the SdH effect can be proposed, such as a distortive structural transition,[8,9] which may give rise to a random lattice potential, or a low-temperature magnetic ordering transition, for which evidence has been found very recently.[10,11]

It is well known that pressure strongly affects properties of organic metals. One can expect, therefore, that studies of the Cu[N(CN)$_2$]Br compound under pressure would provide information on its electronic properties, in particular, on its FS. In this paper we report an observation of the SdH effect of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br under pressure of $\approx$9 kbar. This finding provides evidence for the normal Fermi-liquid character of the conducting system in the compound and proves the high quality of the crystals. The results are compared with those obtained previously on the Cu(NCS)$_2$ salt and the theoretically predicted FS.

The crystal used in the experiment was grown electrochemically as described elsewhere[12] and had the shape of a thick distorted hexagonal plate of the size $\sim0.5\times0.3\times0.15$ mm^3 with its face parallel to the crystal's highly conducting plane (*ac* plane). The interplane resistance was measured by a standard four-probe ac technique with the relative accuracy to better than 10^{-4} for a typical sample resistance of $\sim$1 Ω. Quasihydrostatic pressure was applied using a piston-cylinder clamp cell with the mineral oil GKZh-94 as a pressure medium. The pressure was estimated from the applied loading force at room temperature and corrected for low temperatures according to Ref. 13. The highest applied load corresponded to 11.3 kbar at room temperature and $\sim$9 kbar at 4.2 K. The accuracy of such an estimation is believed to be within 10%. The magnetic field up to 17 T was generated by a superconducting magnet. The pressure cell was mounted into a rotation unit which could be rotated *in situ* with respect to the magnetic field inside the bore of 50-mm diameter.

The room-temperature resistance of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br remarkably drops with increasing pressure, being at 10 kbar an order of magnitude as small as its ambient pressure value. The dependence is gradual and shows no discontinuities, which could be attributed to a

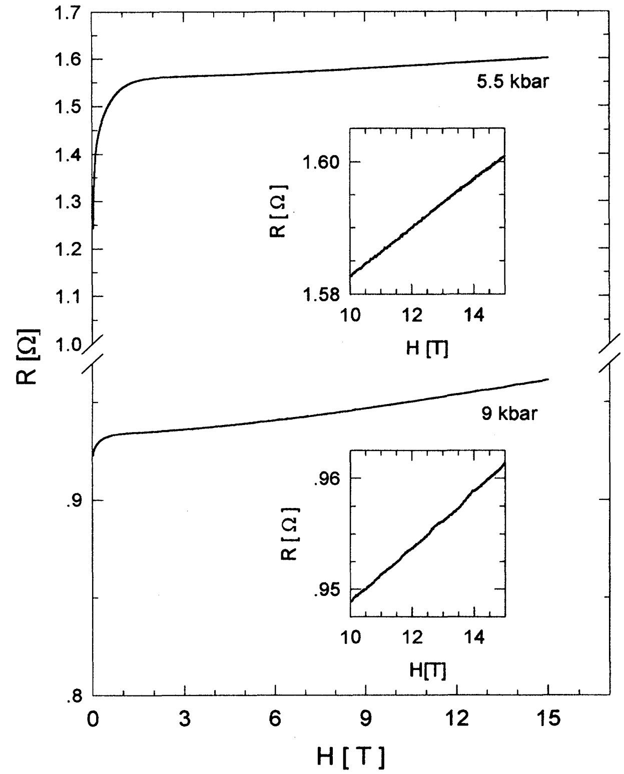

FIG. 1. Interlayer resistance of κ-(BEDT-TTF)$_2$ Cu[N(CN)$_2$]Br vs magnetic field at various pressures at 1.45 K. The magnetic field is applied normal to the *ac* plane.

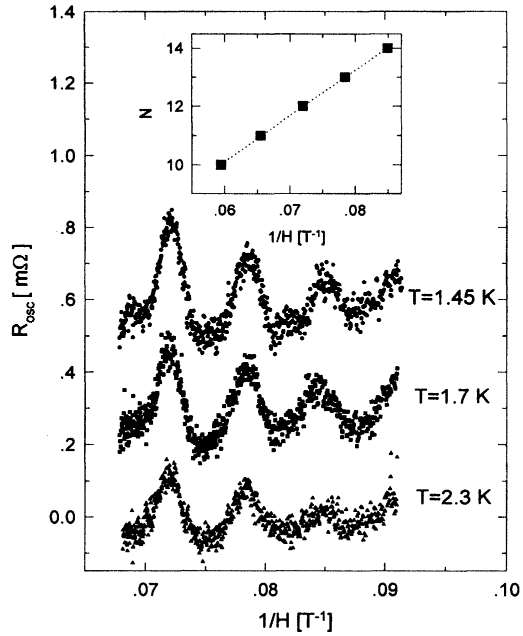

FIG. 2. Oscillatory component R_{osc} of MR vs inverse magnetic field $1/H$ at different temperatures. Inset shows the resistance peak periodicity vs inverse magnetic field, where N is the number of the peak.

phase transition, up to the highest pressure, 11.3 kbar. The high pressure resistance shows a monotonous metallic behavior upon cooling; the resistance peak around 100 K is suppressed by pressure, in agreement with the previous report.[14] Figure 1 shows the dependence of the low-temperature resistance on the magnetic field normal to the *ac* plane for the pressure, $P \sim 5.5$ and 9 kbar. In contrast to many other BEDT-TTF based metals, the MR is very low; the ratio $\Delta R(H)/R(0) \approx 0.03$ at $H = 15$ T for both pressures, where $R(0)$ is the resistance in the absence of the magnetic field and $\Delta R(H)$ is the resistance increment for the magnetic field H. The low field parts of the curves reveal the onset of superconductivity (more correctly, the presence of superconducting fluctuations) even at these high pressures, although the bulk superconductivity is expected to be suppressed above ~4 kbar.[15] At $P \approx 9$ kbar one can resolve weak oscillations of MR starting above 10 T. More clearly the oscillations are shown in Fig. 2 after substracting the monotonic background. The inset in Fig. 2 demonstrates the resistance peak periodicity in scale of inverse field with the period $\Delta(1/H) = 0.006\,42$ T^{-1}. The oscillations become stronger with lowering the temperature, their phase being temperature independent. Based on the periodicity and the temperature dependence, we attribute the oscillations to the SdH effect. The analysis in terms of the standard Lifshitz-Kosevitch theory[16] gives the cyclotron mass $m \approx 0.95 m_0$, where m_0 is the free-electron mass, and the Dingle temperature $T_D \approx 3.5$ K.

Note that the oscillation shape is not sinusoidal. In order to get more information about the harmonic contents, we have performed several field sweeps up to 17 T. An example is shown in Fig. 3. An additional peak is fully reproduced in all the sweeps made at various temperatures. As is seen in the inset of Fig. 3, the fast Fourier transformation taken over the field range from 11 to 17 T yields a very strong second harmonic contribution, in addition to the fundamental one. No higher harmonics have been detected.

The low oscillation frequency and strong relative scatter-

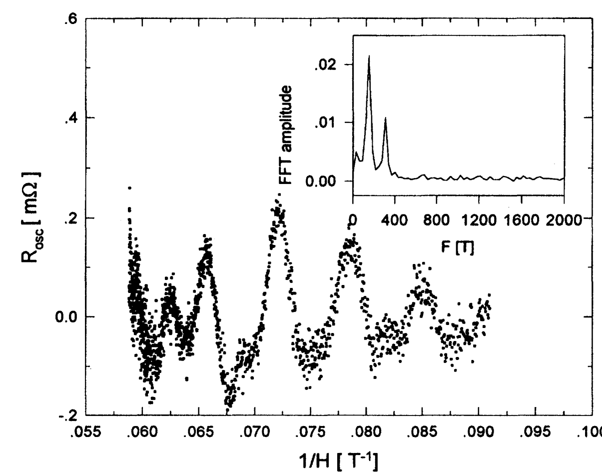

FIG. 3. Oscillatory component R_{osc} of MR vs $1/H$ up to 17 T at 1.45 K. Inset shows the fast Fourier transformation.

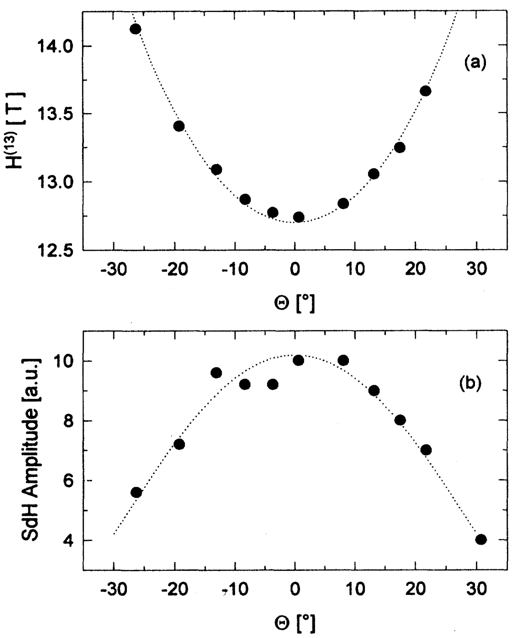

FIG. 4. (a) Angular dependence of the magnetic field giving the 13th peak in the MR oscillations. (b) Angular dependence of the oscillation amplitude for the 13th peak fitted by the LK formula for a cylindrical FS (dashed curve).

ing of the experimental data make the direct determination of the angular dependence of the frequency problematic. However, assuming that the phase offset of the oscillations at $H \rightarrow \infty$ does not vary with Θ, we can follow this dependence by plotting the magnetic field giving the nth peak in MR as a function of the angle Θ. The result for the 13th peak shown in Fig. 4(a) can be fairly fitted by the $1/\cos\Theta$ law, thus indicating the cylindrical shape of the FS. The angular dependence of the oscillation amplitude A is also consistent with the cylindrical FS. This is demonstrated in Fig. 4(b) in which the experimental data are fitted by the Lifshitz-Kosevitch (LK) formula, taking the determined values of $\mu = m/m_0$ and T_D, the g factor $g=2$, and assuming the angular dependence of the cyclotron mass, $m(\Theta) = m(0)/\cos\Theta$.

Regarding the theoretically predicted band structure of κ-(BEDT-TTF)2Cu[N(CN)2]Br, the calculations[7] based on the ambient-pressure crystal structure yield the FS very similar to those obtained for the other κ-(BEDT-TTF)$_2$X salts, with X=Cu(NCS)$_2$,[3] Cu[N(CN)$_2$]Cl,[17] and I$_3$.[18] For all of them the FS is expected to be formed by a linear chain of cylinders with the cross section equal to the Brillouin zone (BZ) area, which are overlapped in the k_c direction giving rise to a holelike cylinder centered in the X point of the BZ boundary and a pair of open electronlike sheets extended along the k_c direction. Among these compounds only the Cu(NCS)$_2$ salt is predicted to possess a considerable gap between the closed and open FS sheets due to the lack of the inversion symmetry in its crystal structure. The SdH oscillations corresponding to the classical (α) and magnetic-breakdown (β) orbits with the cross sections equal to ≈ 16 and 100 % of the BZ area, respectively, confirm the predicted picture of the FS in Cu(NCS)$_2$.[4] In the salt with X=I$_3$ the β-orbit oscillations become visible starting from lower field (~ 5 T) and they are stronger than the α-orbit oscillations above 7–9 T,[19] indicating that the gap is indeed considerably smaller than in the Cu(NCS)$_2$ salt.

At first sight, the oscillations found in the present compound can be attributed to the holelike cylinder as in the α-orbit oscillations in the above two salts. However, the frequency is much lower in our case, corresponding to only $\approx 4.4\%$ of the BZ area, a factor of 4 smaller than expected from the calculations.[7] Moreover, the β-orbit oscillations are not found up to the highest available field, 17 T, despite the predicted absence of the gap between open and closed FS parts.[20] One can propose that the mentioned discrepancies are associated with the high pressure involved in the present experiment. Indeed, the pressure of 9 kbar may be high enough to induce the lattice deformation leading to a considerable gap at the BZ boundary, thus depressing the β-orbit oscillations. However the large difference between the predicted and observed sizes of the α orbits is difficult to explain by a smooth variation of the crystal lattice parameters under pressure. The calculated [for X=Cu[N(CN)$_2$]Cl (Ref. 17)] and experimentally obtained [for X=Cu(NCS)$_2$ (Ref. 21)] pressure dependencies of the band structure yield only a few percent variation of the FS size at $P \sim 10$ kbar. Therefore, assuming that the ambient-pressure band structure of the Cu[N(CN)$_2$]Br salt is similar to those of the isostructural (BEDT-TTF)$_2$X metals, the present results suggest either an unusually high sensitivity of the electronic system to pressure or a pressure-induced phase transition.

Now we turn to the very low amplitude of the oscillations. Indeed, the obtained ratio $R_{\rm osc}/R \sim 10^{-4}$ ($R_{\rm osc}$ is the oscillatory component of the magnetoresistance) is by 2 orders of magnitude as small as the typical value for the Cu(NCS)$_2$ salt at the same conditions. A reason for that might be low quality of the sample studied, i.e., strong scattering, mosaic structure, or inhomogenious stress. All these factors are expected to result in the exponential decrease of the oscillation amplitude with the exponent in the same form as in the Dingle factor, $\exp(-K/H)$. The observed field dependence yields $K \approx 50$ (corresponding to the Dingle temperature $T_D \approx 3.5$ K), which is quite reasonable for the known organic metals and cannot cause the unusually strong suppression of the oscillatory signal. Another possibility to explain the low amplitude may be a small contribution of the detected FS cylinder into the total conductivity. However, if we assume the FS topology to be the same as for the Cu(NCS)$_2$ salt, the reduction of the cylinder cross section by a factor of 4, the ratio between the SdH frequencies of the two compounds, is hardly supposed to result in the observed low amplitude.

As mentioned above, recent experiments[10,11] give evidence of a low-temperature magnetic-order transition at the ambient pressure. The magnetic order may lead to a highly inhomogeneous local magnetic induction in the sample, thus killing the SdH effect. One can imagine that the low amplitude of the SdH oscillations at 9 kbar is also related to the magnetic ordering which is partially suppressed under this pressure.

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[1] J. M. Williams, K. D. Carlson, U. Geiser, and H. M.-H. Wangbo, *Organic Superconductors: Synthesis, Structure, Properties and Theory* (Prentice Hall, Englewood Cliffs, NJ, 1992).

[2] J. Wosnitza, Int. J. Mod. Phys. B **7**, 2707 (1993).

[3] K. Oshima, T. Mori, H. Inokuchi, H. Urayama, H. Yamochi, and G. Saito, Phys. Rev. B **38**, 938 (1988).

[4] T. Sasaki, H. Sato, and N. Toyota, Physica C **185-189**, 2687 (1991); C.-P. Heidmann, H. Mueller, W. Biberacher, K. Neumaier, C. Probst, K. Andres, A. G. M. Jansen, and W. Joss, Synth. Met. **41-43**, 2029 (1991).

[5] M. V. Kartsovnik, G. Yu. Logvenov, T. Ishiguro, W. Biberacher, and H. Anzai (unpublished).

[6] M. V. Kartsovnik, A. E. Kovalev, V. N. Laukhin, H. Ito, T. Ishiguro, N. D. Kushch, H. Anzai, and G. Saito, Synth. Met. **70**, 819 (1995).

[7] A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoort, J. E. Thompson, D. L. Stupka, D. Jung, and M.-H. Whangbo, Inorg. Chem. **29**, 2555 (1990).

[8] Y. Nogami, J. P. Pouget, and T. Ishiguro, Solid State Commun. **89**, 113 (1993).

[9] M. Kund, H. Muller, W. Biberacher, K. Andres, and G. Saito, Physica B **191**, 274 (1993).

[10] U. G. L. Lahaise, Q. Chen, L. E. DeLong, C. P. Brack, H. H. Wang, K. D. Carlson, J. A. Schlueter, and J. M. Williams, Phys. Rev. B **51**, 3301 (1995).

[11] K. Andres, H. Posselt, P. Christ, M. Kund, and W. Biberacher (unpublished).

[12] T. Komatsu, N. Matsukawa, T. Nakamura, H. Yamochi, G. Saito, H. Ito, and T. Ishiguro, Phosphorus Sulfer Silicon **67**, 295 (1992).

[13] J. D. Thompson, Rev. Sci. Instrum. **55**, 231 (1984).

[14] Yu. V. Sushko, V. A. Bondarenko, R. A. Petrosov, N. D. Kushch, and E. B. Yagubskii, Physica C **185-189**, 2683 (1991).

[15] J. E. Schirber, D. L. Overmyer, J. M. Williams, A. M. Kini, and H. H. Wang, Physica C **170**, 231 (1990).

[16] D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge University Press, Cambridge, 1984).

[17] A. J. Schultz, H. H. Wang, J. M. Williams, L. W. Finger, R. M. Hazen, C. Rovira, and M.-H. Wangbo, Physica C **234**, 300 (1994).

[18] K. Kajita, Y. Nishio, S. Moriyama, W. Sasaki, R. Kato, H. Kobayashi, and A. Kobayashi, Solid State Commun. **64**, 1279 (1987).

[19] D. Schweitzer, E. Balthes, S. Kahlich, I. Heinen, H. J. Keller, W. Strunz, W. Biberacher, A. G. M. Jansen, and E. Steep, Synth. Met. **70**, 857 (1995).

[20] Very recently, β-orbit oscillations of the expected frequency, $\approx$4000 T, have been found under pressure at higher fields, above 24 T, by; M. Kartsovnik, W. Biberacher, P. Christ, E. Steep, A. G. M. Jansen, and H. Muller (unpublished).

[21] J. Caulfield, W. Lubczynski, F. L. Pratt, J. Singlenton, D. Y. K. Ko, W. Hayes, M. Kurmoo, and P. Day, J. Phys. Condens. Matter **6**, 2911 (1994).