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CONDENSED MATTER

Hydrostatic-Pressure-Induced Reentrance of the Metallic State in the κ-$(ET)_2Hg(SCN)_2Cl$ Quasi-Two-Dimensional Organic Conductor

R. B. Lyubovskii[a], S. I. Pesotskii[a, *], V. N. Zverev[b], E. I. Zhilyaeva[a], S. A. Torunova[a], and R. N. Lyubovskaya[a]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia*

[b] *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia*

**e-mail: pesot@icp.ac.ru*

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On cooling below 30 K, the κ-$(ET)_2Hg(SCN)_2Cl$ quasi-two-dimensional organic metal, which is in the quantum spin liquid state at liquid helium temperatures, undergoes a transition to the Mott insulator state. The application of a hydrostatic pressure $p = 0.7$ kbar stabilizes the metallic state and makes it possible to study the behavior of the interlayer magnetoresistance at liquid helium temperatures. The field dependence of the magnetoresistance exhibits an unlimited power-law growth, which indicates that the polaron mechanism contributes to the interlayer transport. The spectrum of observed magnetoresistance oscillations corresponds to the Fermi surfaces characteristic of conducting layers with the κ-type structure.

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In the early 1970s, a novel state of solids, namely, quantum spin liquids, was theoretically predicted [1]. This prediction was actually confirmed in experiment only 40 years later in the study of the synthetic mineral herbertsmithite [2], which can exhibit the characteristics predicted for the spin liquid. In this compound, neither a long-range magnetic order nor structures such as spin glass were found down to such ultralow temperatures as 50 mK. Having a nontrivial frustrated lattice, these materials contain triangular motifs involving triangles with magnetic atoms located at their vertices. Such structure prevents the formation of long-range order. Because of quantum fluctuations and strong correlations between spins, frustrated magnets remain disordered even near absolute zero [3–6].

Low-dimensional organic conductors form a large class of compounds with various unusual states and a number of phase transitions [7, 8]. Modern chemical synthesis makes it possible to produce organic conductors (metals) with strongly correlated electrons. According to theoretical predictions, quantum fluctuations for such materials become important at very low temperatures. These fluctuations can lead to the appearance of "quantum spin liquid" states and manifest themselves in different physical properties [9, 10].

The existence of a spin liquid state has already been confirmed in a number of organic metals based on bis(ethylenedithio)tetrathiafulvalene (ET), which are characterized by the phase transition to the Mott insulator [11, 12]. In isostructural quasi-two-dimensional organic metals κ-$(ET)_2Hg(SCN)_2X$ (X = Cl, Br), phase transitions are observed on cooling at temperatures of 30 and 80 K, respectively. In these compounds, the conducting organic layers consist of dimers of ET molecules and alternate with nonconducting layers of inorganic $Hg(SCN)_2X$ anions. The dimers of ET molecules in the conducting layers are almost perpendicular to each other (the κpacking type) and are connected by a large number of shortened S...S bonds [13, 14].

In this work, the electron system of a metallic state in a highly frustrated quasi-two-dimensional κ-$(ET)_2Hg(SCN)_2Cl$ organic conductor is experimentally studied for the first time by analyzing the behavior of the magnetoresistance. At temperatures above 30 K, this compound behaves like a metal with a half-filled band with strong electron–electron correlations. Near $T = 30$ K, the material exhibits a metal–insulator transition, and the charge disproportionation occurs inside the dimers of ET molecules, which leads to the formation of a long-range order. However, as the temperature drops below 15 K, the long-range order disappears completely, and the system transforms to the quantum spin liquid state [15]. Bis(ethylenedithio)tetrathiafulvalene-based organic conductors

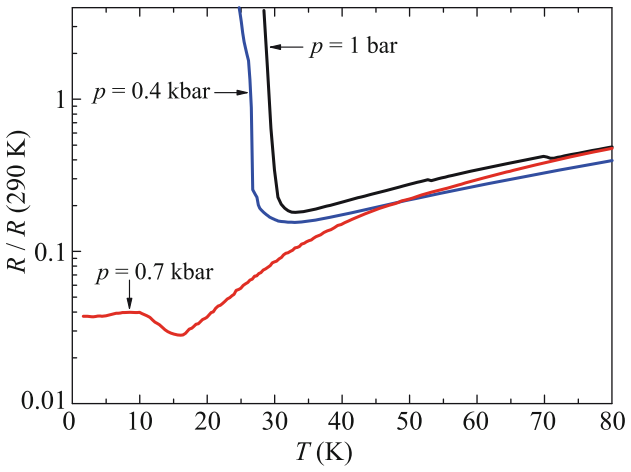

Fig. 1. (Color inline) Temperature dependence of the relative interlayer electrical resistance of κ-$(ET)_2Hg(SCN)_2Cl$ at different applied pressures.

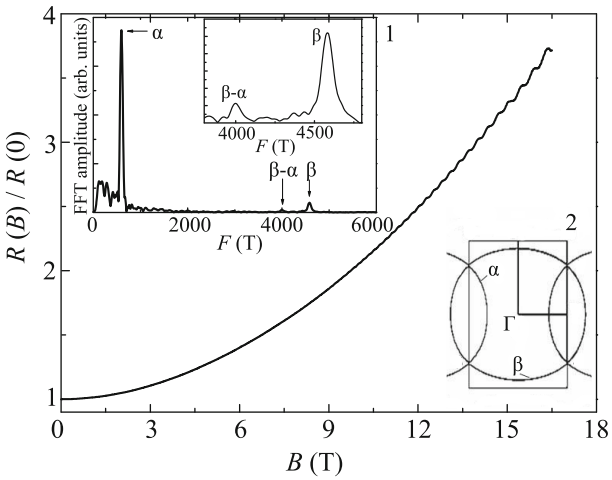

Fig. 2. Magnetic field dependence of the longitudinal magnetoresistance in κ-$(ET)_2Hg(SCN)_2Cl$ at $T = 0.47$ K and $p = 0.7$ kbar. The upper inset shows the Fourier spectrum of the magnetoresistance oscillations. The lower inset shows the schematic image of the Fermi surface characteristic of κ-type two-dimensional metals.

are fairly plastic materials, and the applied high pressure can significantly change the conduction band and affect their physical properties [7, 8]. The application of a relatively low external pressure stabilizes the metallic state down to the lowest temperatures and makes it possible to analyze the behavior of the magnetoresistance in the aforementioned conductor.

In our study, we used κ-$(ET)_2Hg(SCN)_2Cl$ single crystals having the shape of irregular parallelepipeds with average dimensions of 1 × 0.3 × 0.02 mm. The conducting layers were perpendicular to the short edge of the crystal; the ac measuring current was applied in the same direction and the interlayer resistance was measured. The magnetoresistance was studied at the applied dc magnetic field up to 16.5 T. The direction of the field always coincided with that of the measuring current. Thus, the longitudinal interlayer magnetoresistance was studied. To create pressure, we used a high-pressure chamber with a hydrophobic organosilicon liquid (HSC) as a transmission medium.

In Fig. 1, we show the temperature dependences of the relative interlayer electrical resistance of κ-$(ET)_2Hg(SCN)_2Cl$ at different pressures. At atmospheric pressure, the sample exhibits a metallic behavior of the interlayer resistance in the range from room temperature to about 30 K. Below this temperature, a rather abrupt metal–insulator transition is observed. The pressure $p \approx 0.4$ kbar shifts the metal–insulator transition by several degrees toward low temperatures. However, the pressure $p \approx 0.7$ kbar completely suppresses the transition and transforms the sample to the metallic state, which is retained down to the lowest temperatures. The presented results are in a good agreement with the previously published phase diagram of this compound [16]. Note that a slight nonmonotonicity in the behavior of the interlayer resistance at $p \approx 0.7$ kbar at low temperatures suggests the proximity of the phase transition at this pressure.

In Fig. 2, we show the magnetic field dependence of the longitudinal magnetoresistance in κ-$(ET)_2Hg(SCN)_2Cl$. In the field $B \approx 16$ T, the resistance grows by about a factor of four and is well described by the relation $R(B)/R(0) = a + bB^{1.9}$ in the whole magnetic field range without any signs of saturation at the highest fields. This behavior is not typical of most quasi-two-dimensional organic metals [17]. One of the possible mechanisms of this behavior may be the formation of polarons around electrons localized by the magnetic field in conducting layers. An increase in the field enhances the degree of localization and, accordingly, increases the height of the Coulomb barrier, which an electron must overcome to pass to an adjacent layer [18]. Beginning with magnetic fields $B \sim 10$ T, the field dependence of the magnetoresistance (Fig. 2) exhibits Shubnikov–de Haas oscillations, which confirm the metallic state of the electron system at low temperatures. The spectrum of such oscillations is shown in Fig. 2 (upper inset). Taking into account the κ type of packing of ET molecules in conducting layers of κ-$(ET)_2Hg(SCN)_2Cl$ [14], we could expect at low temperatures the usual shape of the Fermi surface characteristic of this packing type [19]. It is shown schematically in the lower inset of Fig. 2. Indeed, the Fourier spectrum contains two clearly pronounced frequencies $F_\alpha \approx 600$ T and $F_\beta \approx 4600$ T, corresponding to the orbits covering 13% and 100% of the area of the first Brillouin zone, respectively. The cyclotron masses associated with these frequencies and calculated from the temperature dependences of the oscillation amplitude are $m_\alpha = (2.8 \pm$

$0.1)m_0$ and $m_\beta = (5.2 \pm 0.2)m_0$, where m_0 is the free electron mass. The existence of α and β frequencies is also due to a small gap arising at the points of intersection of the Brillouin zone with the initial Fermi surface, covering the entire area of this zone (two electrons per unit cell). As a result, a closed hole orbit α and two sheets of an open electron orbit are formed. Magnetic breakdown and, as a consequence, the transition of an electron from the α orbit to open areas lead to the formation of a closed β orbit of the magnetic breakdown type. In addition to the fundamental frequencies, the spectrum contains the combination frequency $F_{\beta-\alpha} = F_\beta - F_\alpha \approx 4000$ T, which is not clearly pronounced. This frequency does not correspond to an allowed closed orbit and is caused by the effect of quantum interference [19]. This is confirmed by the value of the cyclotron mass $m_{\beta-\alpha} \approx (2.5 \pm 0.3)m_0 \sim m_\beta - m_\alpha$ related to such frequency.

Thus, the application of a low external hydrostatic pressure $p = 0.7$ kbar suppresses the transition to the insulating state in the quasi-two-dimensional κ-$(ET)_2Hg(SCN)_2Cl$ organic metal and restores the metallic electron structure of the cation layers with the Fermi surface characteristic of the κ-type packing. The power-law increase in the magnetoresistance with the applied magnetic field can be a signature of the contribution of the polaron mechanism to the interlayer transport.

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REFERENCES

1. P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).
2. T.-H. Han, J. S. Helton, Sh. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, and Y. S. Lee, Nature (London, U.K.) **492**, 406 (2012).
3. J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, Phys. Rev. Lett. **98**, 107204 (2007).
4. P. Mendels and F. Bert, J. Phys. Soc. Jpn. **79**, 011001 (2010).
5. M. A. de Vries, K. V. Kamenev, W. A. Kockelmann, J. Sanchez-Benitez, and A. Harrison, Phys. Rev. Lett. **100**, 157205 (2008).
6. J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Qiu, D. G. Nocera, and Y. S. Lee, Phys. Rev. Lett. **104**, 147201 (2010).
7. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, and M. H. Whangbo, *Organic Superconductors (Including Fullerenes) Synthesis, Structure, Properties and Theories* (Prentice Hall, Englewood Cliffs, N.J., 1992).
8. T. Ishiguro, K. Yamaji, and G. Saito, *Organic Superconductors* (Springer, Berlin, 1998).
9. L. Balents, Nature (London, U.K.) **464**, 199 (2010).
10. B. J. Powell and R. H. McKenzie, Rep. Prog. Phys. **74**, 056501 (2011).
11. K. Shimizu, K. Miyagawa, M. Kanoda, M. Maesato, and G. Saito, Phys. Rev. Lett. **91**, 107001 (2003).
12. N. Hassan, S. Cunningham, M. Mourigal, E. I. Zhilyaeva, S. A. Torunova, R. N. Lyubovskaya, J. A. Schlueter, and N. Drichko, Science (Washington, DC, U. S.) **360**, 1101 (2018).
13. R. B. Lyubovskii, R. N. Lyubovskaya, and O. A. Dyachenko, J. Phys. (France) **6**, 1609 (1996).
14. N. Drichko, R. Beyer, E. Rose, M. Dressel, A. Schlueter, S. A. Turunova, E. I. Zhilyaeva, and R. N. Lyubovskaya, Phys. Rev. B **89**, 075133 (2014).
15. N. M. Hassan, K. Thirunavukkuarasu, Z. Lu, D. Smirnov, E. I. Zhilyaeva, S. Turunova, R. N. Lyubovskaya, and N. Drichko, npj Quantum Mater. **5**, 15 (2020).
16. A. Lohle, E. Rose, S. Singh, R. Bayer, E. Tatra, T. Ivek, E. I. Zhylyaeva, R. N. Lyubovskaya, and M. Dressel, J. Phys.: Condens. Matter **29**, 055601 (2017).
17. P. D. Grigoriev, Phys. Rev. B **88**, 054415 (2013).
18. P. D. Grigoriev, Phys. B (Amsterdam, Neth.) **407**, 1932 (2012).
19. M. V. Kartsovnik, Chem. Rev. **104**, 5737 (2004).

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