

About the paper "NORMAL-PRESSURE SUPERCONDUCTIVITY IN ORGANIC METAL (BEDT-TTF)₂I₃ [BIS(ETHYLENEDITHIOLO)TETRATHIAFULVALENE TRIIODIDE]" by E.B. Yagubskii, I.F. Schegolev, V.N. Laukhin, P.A. Kononovich, M.V. Kartsovnik, A.V. Zvarykina and L.I. Buravov (1984) .

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The paper [1] is a result of a 17-year purposeful search for organic superconductors. In 1966 Igor F. Schegolev put together a team consisting of physicists, chemists and crystallographers at the Branch of Moscow Institute of Chemical Physics in Chernogolovka, and set them the task to create organic superconductors. The impetus to this task had been a work by the American physicist-theorist W.A. Little. In 1964 W.A. Little proposed a new electron-electron (exciton) mechanism of superconductivity and a hypothetical high-temperature superconducting macromolecule to realize this mechanism. Little's model involves a linear conducting polyene chain, which contains easily polarizable substituents. Electron vibrations in such substituents were expected to provide effective attraction between conduction electrons resulting in superconductivity with high critical temperature T_c . Though arguments and calculations of W.A. Little were not quite rigorous, his work attracted great attention. This is quite understandable since at that time the traditional direction associated with the design of superconducting alloys was almost exhausted. Despite consolidated efforts of physicists, metallurgists and materials scientists, critical temperature of superconducting transition, reaching 18K, has not grown for the past 15 years. Moreover, some publications claimed in theory that the phonon mechanism realized in conventional superconductors could not provide T_c higher than 30 -40 K. We faced the problem of choosing the objects to be studied. It should be noted, however, that at that time not that superconductors, but even normal organic metals did not exist, and the problem of possible states in linear electron systems was far from being clear. Schegolev made a choice in favour of conducting molecular crystals rather than conducting polymers. It was supposed that the search for organic superconductors would be long and could be successful only through the successive analysis of a correlation between structure and electron properties. Now it is obvious that such strategy was valid. Organic superconductors were found in early 80ies among molecular crystals, while polymeric organic superconductors have not been obtained so far. At initial stage of our research we concentrated on the crystals of tetracyanoquinodimethane (TCNQ) radical anion salts, which had been synthesized in the USA shortly

before, and some of them had shown essentially high room-temperature conductivity ($\approx 100 \text{ Ohm cm}^{-1}$). However, physical properties of the salts were practically unstudied. Planar TCNQ molecules easily accept one electron to form stable radical anions packed above each other in the crystals of TCNQ salts to form continuous stacks. Anisotropic character of wave functions of π -electrons gives rise to a noticeable overlapping of molecular orbitals in the direction perpendicular to the plane of TCNQ molecules and, as a result, to sufficient room-temperature conductivity along the stacks, while conductivity in transverse directions is several orders of magnitude lower. So form the quasi-one-dimensional conducting chains in which electric current can flow in one direction, as in the hypothetical polymer Little molecule. However, by the middle 70ies the study of quasi-one-dimensional conductors clearly showed that one-dimensional systems are unfavorable for the design of superconductors because of very strong dielectric instabilities, first of all those associated with the effect of disordering and the Peierls metal-insulator transition. To attain superconductivity, one had to give up one-dimensionality. Higher overlapping of electron wave functions of molecules from the neighboring stacks was required to provide more than one direction for electron motion. In 1977 we synthesized a radical cation salt, tetraselenotetracene chloride, (TSeT)₂Cl, which up to now has a record room-temperature conductivity among organic molecular compounds ($\approx 2.5 \cdot 10^3 \text{ Ohm cm}^{-1}$ along the TSeT stacks). The presence of four large selenium atoms in the TSeT molecule provides certain overlapping of wave functions of π -orbitals in the transverse direction (across the stacks). As a result, electron motion is "not so one-dimensional and a metal-semimetal transition rather than a metal-dielectric one is realized in (TSeT)₂Cl at low temperature (27K). A year later it was found that the transition is suppressed by applying low pressure of 4.5 kbar to the (TSeT)₂Cl crystals, and the compound retains metallic properties ($\approx 10^5 \text{ Ohm cm}^{-1}$ at 4.2 K). Though this first really stable organic metal appeared to be non-superconducting, the existence of a stable metallic state in organic compounds implied that organic superconductivity is possible. Metals tend to become superconductors. So it happened soon. In 1979 K. Bechgaard from the Hans Christian Ørsted Institute in Copenhagen synthesized a radical cation

salt based on another selenium containing donor, tetramethyltetraselenafulvalene, of $(\text{TMTSeF})_2\text{PF}_6$ composition, which showed a metal-insulator transition at very low temperature (12 K). In 1980 the group of D. Jerome from the University of Paris-Sud found that this transition is fully suppressed at 11 kbar pressure, and $(\text{TMTSeF})\text{PF}_6$ undergoes a superconducting transition at 0.9 K. Thus, the first organic superconductor was found. In 1981-1983 six more superconductors based on TMTSeF salts with octahedral and tetrahedral anions were found, and there was only one superconductor at ambient pressure, tetramethyltetraselenafulvalene perchlorate, $(\text{TMTSeF})_2\text{ClO}_4$, with $T_c = 1.2$ K. However, soon it became clear that the family of organic superconductors based on TMTSeF salts is quite narrow. All seven superconductors of the TMTSeF family are isostructural and show low values of T_c (1-2 K). The attempts to extend the number of superconductors by varying counter ions in the TMTSeF salts turned unsuccessful. The next principally important step in the field of organic superconductivity was made in Chernogolovka. In 1983 we synthesized the first quasi-two-dimensional organic superconductor at ambient pressure, bis(ethylenedithio)tetrathiafulvalene triiodide, $(\text{BEDT-TTF})_2\text{I}_3$ with $T_c = 1.4$ K. Unlike quasi-one-dimensional superconductors of the TMTSeF family, $(\text{BEDT-TTF})_2\text{I}_3$ has a quasi-two-dimensional Fermi surface. In the structure of the salt, BEDT-TTF radical cation layers alternate with the layers formed by I_3 anions. Conductivity in the BEDT-TTF layers is nearly isotropic, while in the direction perpendicular to the layers it is three orders of magnitude lower. The increase in the electron dimensionality of BEDT-TTF salts is due to structural features of this donor molecule: the presence of many sulfur atoms (eight) and noncoplanar terminal CH₂-CH₂ groups. Sulfur atoms provide interaction between stacks, while noncoplanar CH₂-CH₂ groups generate certain steric hindrances for the interactions between the radical cations inside the stacks. Soon we found that a new superconducting state with $T_c = 8$ K emerges in the $(\text{BEDT-TTF})_2\text{I}_3$ crystals under

low pressure (≈ 0.5 kbar). Later on, we succeeded in stabilizing this phase at normal pressure. It was found also that in contrast to the $T_c = 1.4$ K phase which has a structural disorder associated with the arrangement of terminal CH₂-CH₂ groups, the phase with $T_c = 8$ K is completely ordered.

The discovery of quasi-two-dimensional organic superconductors strongly affected the trend of search for organic superconductors and provided a rapid development of chemistry of BEDT-TTF derivatives and the synthesis of multiple related salts with various anions. Now the number of organic superconductors of the BEDT-TTF family is more than one hundred, and T_c grew up to 12.6 K. Regarding the crystal and electronic structure and some properties (low concentration of charge carriers, mixed oxidation state, high values of upper critical fields, proposed d-wave coupling), layered organic superconductors are close to high-temperature metal oxide superconductors and can be considered as models for the study of superconductivity mechanism in HTSC. It should be noted also that the search for organic superconductivity gave birth to a new class of low-dimensional solids, the study of which provided new important results in different areas of solid state physics, such as metal-dielectric and metal-superconductor transitions, coexistence of superconducting and dielectric transitions, charge and spin density waves, magnetic field-induced phase transitions, quantum spin liquid state, giant quantum and semi-classical oscillations of magnetoresistance and others [2].

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- [1] E.B. Yagubskii, I.F. Schegolev, V.N. Laukhin, P.A. Kononovich, M.V. Kartsovnik, A.V. Zvarykina., L.I. Buravov *Sov. Phys. JETP Lett.* 39, 12 (1984).
- [2] *The Physics of organic superconductors and conductors* Springer Ser. in Materials Science, v. 110. ed. by A.G. Lebed, Springer-Verlag, 2008.