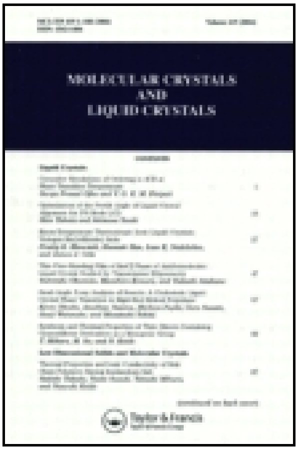

Molecular Crystals and Liquid Crystals

Contribution of the chernogolovka group to chemistry and physics of organic superconductors

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CONTRIBUTION OF THE CHERNOGOLOVKA GROUP TO CHEMISTRY AND PHYSICS OF ORGANIC SUPERCONDUCTORS

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Contribution of the Chernogolovka group to initiating and the development of organic superconductors is reviewed. Particular attention is given to the investigations on the design and synthesis of molecular metals and superconductors. The main steps which have led to discovery of the first quasi two-dimensional organic superconductor at ambient pressure are traced starting with TCNQ salts followed by passing on to tetrachalcogenotetracene ones and then on to the superconductor β-(BEDT-TTF)$_2$I$_3$. The most important results of the last decade are presented as well.

Keywords: organic superconductors; design; TCNQ; TChT; BEDT-TTF salts

INTRODUCTION

In 1966 I. F. Schegolev, now late, has united a team consisting of physicists, chemists and crystallographers at the Institute of Chemical Physics in Chernogolovka, and formulated the task of organic superconductor creation. The Little's theoretical work gave impetus to setting up this problem by Schegolev. As it is known, in 1964 Little suggested an excitonic mechanism of superconductivity and a hypothetic superconducting macromolecule to be synthesized [1]. This macromolecule consists of a linear conducting polymeric chain and easily polarizable groups (cyanine dyes), which have to provide an effective attraction between conducting electrons. However, in the sixties, the problem of possible states of one-dimensional electronic systems was far from being clear. Therefore, the synthesis and study of real quasi one-dimensional conductors were of fundamental importance. Our approach to the problem implied firstly to

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create stable organic metals and afterwards to search for superconductors among them. This approach suggested the study of correlations between the structure and physical properties of organic conductors and then, on this basis, the synthesis of new compounds with the desirable properties. That predetermined our choice of conducting molecular crystals rather than conducting polymers as objects to be studied.

TCNQ SALTS

Only one class of organic molecular compounds with high enough room conductivity ($\sim 100\ \Omega^{-1}\ \mathrm{cm}^{-1}$) has been known in the sixties [2]. Those were radical anion salts based on a strong electron acceptor TCNQ which were built up of linear conducting chains (the TCNQ stacks) regularly packed within a non-conducting matrix of the cations [2,3].

Schegolev's team started with the study of crystals of the TCNQ salts since information on their physical properties was very scanty at that time, in particular, the problem of electronic states at low temperatures in the high-conducting TCNQ salts remained open. Different properties have been investigated including conductivity, magnetic susceptibility, thermopower, specific heat. Schegolev proposed and developed, together with Buravov, an original contactless method for measurements of conductivity and dielectric permeability on small crystals at microwave frequencies [4].

Work on synthesis was carried out in the following directions: obtaining crystals of the known high-conducting TCNQ salts to study their physical properties and synthesis of new TCNQ salts, in particular, with cyanine dye cations as molecular models of Little's superconducting macromolecule [5].

A detailed study of the properties of the high -conducting TCNQ salts with quinolinium, N-methylacridinium and N-methylphenazinium cations showed that their low-temperature electronic state was dielectric [3]. It was detected that the metal-like behavior of conductivity took place only down to about 200 K and there was a significant dispersion between dc and microwave conductivity in the range of low temperatures [3]. Chernogolovka's group was the first to find an interesting peculiarity of a low-temperature state of the quasi one-dimensional conductors, namely, the anomalously high values of dielectric permeability (350—750 at 4.2 K for the TCNQ salts) [3]. The results of the first stage of the investigations were summarized by Schegolev in his review "Electric and magnetic properties of linear conducting chains" [3]. It was supposed that dielectrization of the high-conducting TCNQ salts at low temperatures was a result of localization of electronic states in the TCNQ stacks because of the lattice disordering in these compounds associated with the asymmetry of positive charge on the cations. Therefore, we started searching for cations to synthesize new

TCNQ salts in which positive charge would be delocalized throughout the cation [6,7]. As a result, a novel class of quasi one-dimensional metals based on radical cation salts of tetrachalcogenetetracenes (TChT) was discovered in the seventies [8,9].

TETRACHALCOGENETETRACENE SALTS

Among tetrathiotetracene (TTT) salts obtained, the nonstoichiometric triiodides $(TTT)_2I_{3+\delta}$ $(0 \leq \delta \leq 0.1)$ should be mentioned which have high room conductivity ($10^3\,\Omega^{-1}$ cm^{-1}) along the TTT stacks and exhibit a metal-to-insulator transition at rather low temperatures (45–28 K) [10, 11]. However, by the middle of the seventies, it became evident that one-dimensional conductors were little perspective for the superconductivity search because of their different type dielectric instabilities. One of the synthetic approaches to the increasing dimensionality of organic metals is to replace the S atoms by the larger Se ones in the donor molecules. Our next step was to synthesize tetraselenotetracene (TSeT) salts. The chloride $(TSeT)_2Cl$ is of the greatest interest among the tetrachalcogenetetracene salts. So far, this compound is one of the most conducting molecular organic ones ($\sigma_{rt} \cong 2\text{–}3 \times 10^3\,\Omega^{-1}\text{cm}^{-1}$) [12,13]. Its crystal structure is built up of tetraselenoteracene stacks with considerably shortened interplanar (3.37 Å) and selenium-selenium (3.47 Å) distances [9,13]. There are also shortened distances between Se atoms from different stacks (3.83 Å). In contrast to the typical one-dimensional conductors, a metal-to-semimetal rather than a metal-to-insulator transition takes place in $(TSeT)_2Cl$ crystals at low temperature. Conductivity does not vanish at the temperatures below the conductivity maximum (26 K) but tends to a constant of a order of the room temperature value [8,13]. Laukhin et al. studied conductivity of $(TSeT)_2Cl$ under pressure and found the first order phase transition at $\sim$5 kbar to a new metallic phase which remained stable down to the helium temperature [8,14]. The conductivity of this phase attains $10^5\,\Omega^{-1}\text{cm}^{-1}$ at 4.2 K. Although this first really stable organic metal appeared to be non-superconducting, the fact of a stable metallic state existence in organic compounds indicated that organic superconductivity was possible. As it is known, superconductivity was soon found by Jérome and Bechgaard in the class of radical cation salts based on the other selenium-containing donor, tetramethyltetraselenofulvalene (TMTSF) [15,16]. However, a number of superconductors based on the TMTSF salts is very limited. Except one, they exhibit superconducting transitions only under pressure and have the very low T_c's (1–2 K). In their electronic structure the TMTSF salts are close to quasi one-dimensional conductors and dielectric instabilities are yet strong in them. We continued the search of quasi two-dimensional superconductors.

β_L-(BEDT-TTF)$_2$I$_3$ AND β_H-(BEDT-TTF)$_2$I$_3$ SUPERCONDUCTORS

In 1982 Saito et al. obtained the first quasi two-dimensional organic metal, a radical cation salt of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) with the tetrahedral anion ClO_4 [17]. This work stimulated our search for quasi two-dimensional superconductors among ET salts. We started with the synthesis of ET triiodides. By the middle of 1983 the first crystals of $(ET)_2I_3$ were obtained by the electrocrystallization method. The conductivity study showed that they retained the metallic behaviour down to the helium temperature and underwent a superconducting transition at ambient pressure near 1.5 K [18]. An X-ray analysis showed that the crystals were built up of the ET layers alternating with those of the linear I_3 anions. The cation layers were formed of parallel ET stacks (β-type packing) with a lot of shortened side-by-side $S \cdots S$ contacts [19]. Conductivity was isotropic inside the ET layers, while large anisotropy (of about 10^3) was observed in the perpendicular direction. Thus, the first quasi two-dimensional organic superconductor at ambient pressure was discovered. Upon studying the effects of the crystal synthesis conditions on conducting properties, we found that some crystals of β-$(ET)_2I_3$ exhibited the acceleration of the resistivity fall beginning from ~8 K [20,21]. The application of the magnetic fields suppressed this falling. It allowed us to suggest the existence of one more superconducting phase of $(ET)_2I_3$ with higher T_c. Laukhin et al. studied the behaviour of the β-$(ET)_2I_3$ crystals under pressure and found a drastic change in superconductivity: the increase of T_c up to 8 K at $P \sim 1$ kbar [22]. The T-P phase diagram was investigated and it was found that the β-$(ET)_2I_3$ crystals can exist in two superconducting states: a low-temperature one (β_L) with T_c of 1.5 K and a high-temperature one (β_H) with T_c of 8 K [23,24]. The β_H phase can be retained at ambient pressure by cooling the sample under pressure ($P \geq 400$ bar) followed by the pressure release at low temperatures. On such treatment, the β_H phase exists at atmospheric pressure only at $T < \sim 125$ K. To clarify the differences between β_L and β_H phases, Molchanov et al. studied the crystal structure of β-$(ET)_2I_3$ under pressure of 9 kbar [25]. It was found that the β_H phase was fully ordered in contrast to β_L, in which one of the ET ethylene groups was disordered and an incommensurate lattice modulation arose at low temperature [26]. Chemical methods of stabilization at room temperatures of the β-phase with T_c 7–8 K were developed [27,28]. Thermolysis of the ET polyiodides (ε- and ζ-phases) as well as the

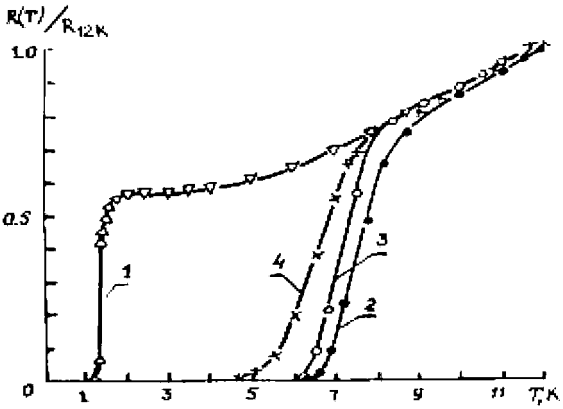

FIGURE 1 Superconducting transition curves for crystals of β-(ET)$_2$I$_3$ obtained by different methods [28]: (1) β_L-(ET)$_2$I$_3$; (2) ε-(ET)$_2$I$_7 \rightarrow \beta_H$-(ET)$_2$I$_3$; (3) ξ-(ET)$_2$I$_{10} \rightarrow \beta_H$-(ET)$_2I_3$; (4) α-(ET)$_2I_3 \rightarrow \beta_H$-(ET)$_2I_3$

annealing of the α-(ET)$_2$I$_3$ phase at about 100 C give rise to β-(ET)$_2$I$_3$ phase with T_c in the range of 6–8 K (Figure 1).

Later on the transformation of α to β-(ET)$_2$I$_3$ was successfully employed by us to prepare the first superconducting polymeric composite films containing thin layers of the β-(ET)$_2$I$_3$ crystals [29,30]. Such a type of composite films with surface layers of oriented microcrystals of molecular conductors based on polyhalogenides or halogenides of ET and its analogs are of great interest because they possess conductivity of metallic type, on the one hand, and on the other hand, retain the advantageous properties of a polymeric matrix such as flexibility, transparency and low density [31,32].

SUBSEQUENT RESULTS

The discovery of quasi two-dimensional superconductors β_L- and β_H-(ET)$_2$I$_3$ gave powerful impetus to the synthesis of new ET salts as well as to the chemical modification of ET molecule itself. As a result, a number of the ET-based superconductors attained 60 and their T_c increased to 12.8 K [33]. Chernogolovka's group made a noticeable contribution to the development of this field. In particular, a lot of new quasi two-dimensional metals were obtained in Chernogolovka. Several superconductors were found among them. I will only dwell on several of the most important results of Chernogolovka's group.

In 1985–1987 Lyubovskaya et al. synthesized the first superconductors based on ET with κ-type layer packing and two incommensurate sublattices: κ-$(ET)_4Hg_{2.89}Cl_8$ ($T_c \cong 1.8$ K at $P \cong 12$ kbar) and κ-$(ET)_4Hg_{2.78}Br_8$ with $T_c \cong 4.3$ K at ambient pressure [34,35].

In the 1990s, a new series of superconductors of the κ-$(ET)_2$-$Cu[N(CN)_2]X$ family with mixed halide anions $X = Br_{0.5}Cl_{0.5}$, $Br_{0.7}Cl_{0.3}$ and $Br_{0.9}I_{0.1}$ with $T_c = 11.3$ K, 11.5 K at ambient pressure and 3.5 K at $P \sim 0.3$ kbar, respectively, was synthesized and the relationship between the anion composition, the disorder in the cation layer and conducting properties was analyzed [36–38].

Chernogolovka's group made the considerable contribution to fermiology of the quasi two-dimensional metals [39]. In particular, Shubnikov-de Haas and angle-dependent magnetoresistance oscillations were for the first time observed in the ET salts by Schegolev's team [40,41].

Of certain interest is also the discovery of a new class of metal complex conductors based on coordination analogs of the ET molecule, $M(dddt)_2$ cation complexes [42–44]. Formally the central C=C bond of ET is substituted by a metal ion in the $M(dddt)_2$ complexes. Although the ET and $M(dddt)_2$ salts often have similar crystal structures, their electronic band structures can be quite different. The reason is that whereas only the HOMO of ET plays role in the conducting bands of its salts, both HOMO and LUMO of $M(dddt)_2$ complexes can be involved in those of their salts [45].

Recently the Chernogolovka team has proposed a new approach to the choice of counter-ions for the synthesis of the ET salts [46]. The approach is based on using metal complex anions exhibiting long-living metastable excited states as counter-ions. It opens the possibility to analyze the influence of the electronic excitation (and the associated geometry changes) of the anions over the conducting (superconducting) electrons. In addition, this approach can also lead to new materials for applications in information storage systems.

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