Organic superconductors

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The properties of superconducting organic compounds are reviewed. Their structure and electronic properties are discussed, as well as the alternative of a dielectric or superconducting transition within a given class of compounds. The problems are discussed of anisotropy of superconducting characteristics, and also the prospects for preparing organic compounds with higher critical temperatures.

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1. INTRODUCTION

The discovery by Jerome *et al.* of superconductivity in the organic compound (TMTSF)$_2$PF$_6$ (tetramethyltetraselenofulvalene hexafluophosphate),[1] and then in a number of related compounds (TMTSF)$_2$X, where X = ClO$_4$, AsF$_6$, SbF$_6$, etc.,[2,3] with a superconducting transition temperature $T_c \approx 0.8$–1.3 K was the successful culmination of goal-directed searches for organic superconductors that took more than 15 years. The studies along this line were stimulated by the paper of Little,[4] which advanced the hypothesis that high-temperature superconductivity could be realized in organic systems of one-dimensional type based on an exciton mechanism (see Ref. 5). Soon Kepler found a number of organic quasi-one-dimensional compounds—the radical-ion salts of tetracyanoquinodimethane (TCNQ), which possessed metallic properties at room temperature. However, the studies of these salts at low temperatures performed by Schchegolev and his associates (see Ref. 6) showed that they transform to the dielectric state on cooling. A subsequent detailed study of organic compounds made it possible to uncover the reasons for loss of metallic properties and to find the way towards attaining the superconducting state.

The tendency of these compounds to a dielectric transition involves the fact that organic molecules of the type of TCNQ are packed in the crystal to form chains or stacks. The collectivized π-electrons move rather well along the stacks, but their motion between chains is hindered. Consequently the motion of the conduction electrons (π-electrons) has a strong anisotropy of one-dimensional type. At the same time, theoretical studies showed that Peierls instability caused by electron-phonon interaction, localization of electrons owing to lattice disorder, and Coulomb interaction of the electrons lead to a dielectric character of the one-dimensional electronic systems (see, e.g., Chap. 7 of Ref. 5, and the literature cited there). Therefore most of the quasi-one-dimensional crystals having good conductivity at room temperature have proved to be Peierls dielectrics at low temperatures. The classical behavior of this type was found in the compound TTF-TCNQ (TTF = tetrathiofulvalene) with a Peierls transition temperature $T_P \approx 55$ K.[7,8]

The mechanisms that lead to a dielectric transition on cooling are weakened if one increases the overlap of the electronic wave functions of neighboring chains, i.e., increases the degree of two-dimensionality or three-dimensionality of electronic motion. The planar molecule TMTSF, which was synthesized by Bechgaard, and which he used to obtain radical-ion salts, proved suitable for obtaining good overlap of the electronic wave functions of neighboring chains. The use of this molecule, which contains four selenium atoms in the conjugation chain, led to obtaining the first organic superconductors[1] (se the review of Ref. 87).

After the discovery of superconductivity in the class of compounds (TMTSF)$_2$X, the list of organic superconductors was supplemented by representatives of a new class (BEDT-TTF)X. The molecule BEDT-TTF (bisethylenedithiolotetrafulvalene) has eight atoms of sulfur in the conjugation

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[1)]Before this, superconductivity in a system containing no metal atoms had been found by Green *et al.*[9] in the polymeric compound polysulfur nitride (SN)$_x$ at temperatures $T < T_c \approx 0.26$ K. The anisotropy of electronic properties of this compound is small, and it lacks the dielectric transitions inherent in the quasi-one-dimensional systems.

chain, and going from TMTSF to BEDT-TTF made it possible to create organic compounds with even lesser anisotropy. In the salt (BEDT-TTF)$_4$(ReO$_4$)$_2$ Parkin et al.[10] found superconductivity at pressures above 4 kbar and $T < T_c \approx 1.5$–2 K. The salts of BEDT-TTF with I obtained by Yagubskiĭ yielded a superconducting transition at $T_c \approx 3$ K without applying external pressure.[11,12]

Below we shall take up in detail the structure and electronic properties of the superconducting radical-ion salts in comparison with the compounds (SN)$_x$ and TTF-TCNQ. We shall pay special attention to the dielectric and superconducting transitions in these compounds and the "dielectric or superconductor" alternative as applied to this class of quasi-one-dimensional compounds. We shall also discuss the problem of the dimensionality of the superconducting characteristics of these systems and the prospects for obtaining organic compounds having higher critical temperatures.

2. STRUCTURE AND ANISOTROPY OF MOTION OF ELECTRONS IN THE NORMAL METALLIC STATE OF THE COMPOUNDS (TMTSF)$_2$X and (BEDT-TTF)X

a) (TMTSF)$_2$X complexes

In (TMTSF)$_2$X crystals, the planar TMTSF molecules form stacks (along the a axis) separated by chains of acceptor molecule-anions X in the direction of the c axis (Fig. 1a). Equivalent chains are repeated along the b axis (Fig. 1b), so that, as a whole, the system amounts to alternating parallel layers of chains of TMTSF and X. Within the layers the chains of identical donor and acceptor molecules lie parallel to one another.[13]

The overlap of the electronic wave functions of the TMTSF molecules in the direction perpendicular to the plane of the molecules, i.e., along the a axis, yields a width of the conduction band of about 1.2 eV according to the experimental data on the position of the plasma edge in the compound with X = PF$_6$,[14] according to the data on the density of electronic states. The measurements of the heat capacity of (TMTSF)$_2$ClO$_4$ at low temperatures performed by Garoche et al.[15] enable one to find the coefficient γ of the term linear in the temperature in the heat capacity. It corresponds to a density of electronic states $N(0) = 1.05$ states/eV·spin per molecule of TMTSF. The width W_a of the band in the strong-coupling approximation is determined from the data for $N(0)$ by using the relationship

$$N(0) = \frac{4}{\pi W_a \sin(\pi p/2)}. \tag{1}$$

Here p is the degree of occupancy in the band.

The analysis of the electron-density distribution in the TMTSF molecules and the analysis of the crystallographic data by Wudl[16] show that the strong overlap of the electronic wave functions of the neighboring TMTSF molecules within the chains comes mainly from the electrons of the Se atoms, rather than the π-electrons of the carbon atoms. It is precisely the former that give rise to an electronic band about 2.5 times broader than the band in chains made of TCNQ molecules, which contain π-electrons but lack Se atoms. Moreover, the Se atoms produce a rather good overlap of the wave
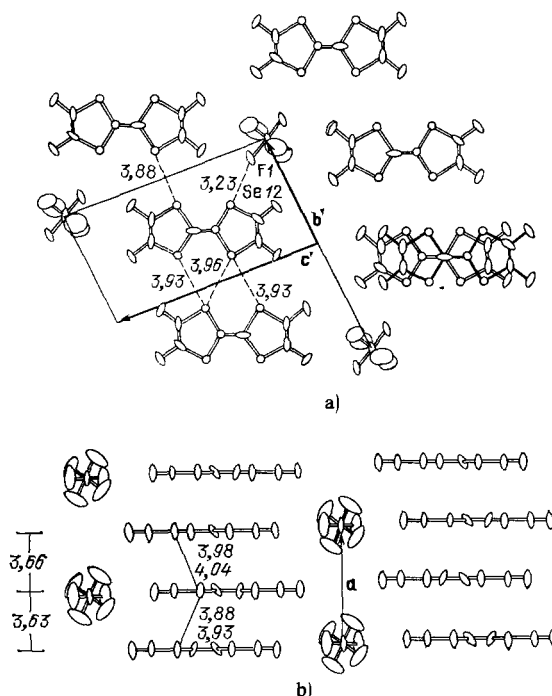

FIG. 1. a) View of the structure of (TMTSF)$_2$PF$_6$ along the a axis; b) view of the structure of (TMTSF)$_2$PF$_6$ along the b axis.

functions of molecules from neighboring chains along the b axis (Fig. 1a). For almost all the pairs of selenium atoms from neighboring TMTSF molecules along both the a and b axes, the Se–Se distance (3.9 Å) is smaller than the van der Waals radius of selenium atoms (4 Å). Consequently the structure of selenium and carbon atoms allows electrons to move rather freely in the a,b plane. Here the motion of the electrons passes via the carbon atoms only within the TMTSF molecules.

Measurements of the anisotropy of conductivity and of the upper critical magnetic field H_{c2} confirm these conclusions. The conductivity σ_a along the chains of 20 K amounts to 10^5–10^6 ohm^{-1} cm^{-1}; at room temperature $\sigma_a \approx 10^3$ ohm^{-1} cm^{-1}. The conductivity σ_b along the b axis is only 25-fold smaller than σ_a.[13,17,18]. Measurements of the upper critical magnetic field for the superconducting transition indicates that the anisotropy of motion of electrons in the a,b plane in the superconducting phase proves even smaller (see Sec. 5). We can explain this with the idea that structural inhomogeneities cause the observed anisotropy of the conductivity to deviate from the true anisotropy of electronic properties of the ideal structure. The data on the orientational dependence of H_{c2} in principle are free from this defect. However, if the superconducting transition is observed under pressure (as in (TMTSF)$_2$PF$_6$), then the corresponding measurements involve great technical difficulties owing to the need of very exact orientation when the anisotropy of H_{c2} is strong.

An alternative possibility of obtaining information on the character of the electronic spectrum is offered by studying the rate of NMR relaxation as a function of the magnetic field: $T_1^{-1}(H)$.[19] In principle, the corresponding experi-

TABLE I.

Compound	Conductivity $\sigma_\parallel$ along the chains, ohm⁻¹. cm⁻¹	σ_a/σ_b	σ_b/σ_c	H_c, kOe/K	H'_c, kOe/K	H_a, kOe/K	$N(0)$, erg⁻¹ cm⁻¹	T_c, K
TTF—TCNQ [23]	300—500 ($T=300$ K)	$(350—500)^{-1}$ ($T=300$ K)	120 ($T=300$ K)				~$0.1 \cdot 10^{34}$	
(SN)$_x$	$\sigma_b = 5\cdot10^5$ ($T=4$ K)[84]		$5\cdot10^4$ ($T=4$ K)[84]	4.2_{78}	30_{78}	3.8_{78}	$0.35\cdot10^{14}$ / 8	0,3
(TMTSF)₂ClO₄ —R [15]	$10^5—10^6$ ($T=20$ K)	25 [18] ($T=300$ K)	$—20$ [22]	1.1	16	48	$0,23\cdot10^{34}$	1,3
(TMTSF)₂PF₆, $P=11$ kbar	$4\cdot10^5$ ($T=4$ K)[1,3]			0.3_{17}	$1,5_{15}$	$1,9_{15}$		1,3
(TMTSF)₂AsF₆, $P=9.5$ kbar	10^6 ($T=4$ K)[49]			1	14			1,3
(BEDT—TTF)₂(ReO₄)₂ [10]	200 ($T=300$ K)		20	0,5	1			2
(BEDT—TTF)₂I₃ [11]	$3\cdot10^3$			0,2	15	20	~$1\cdot10^{34}$	3

mental dependence enables one to determine the transverse transition integrals.[19,20] Experiments of this type have been performed for the salt (TMTSF)₂PF₆,[21] and this compound exhibits a dependence of T_1^{-1} on H starting with fields of 12 kOe and logarithmic in type ($T_1^{-1} \sim \ln H$) up to fields of 110 kOe. This behavior indicates a two-dimensional character of the anisotropy of the electronic spectrum. In the case of a one-dimensional anisotropy of electronic motion, one should observe a $T_1^{-1} \sim H^{1/2}$ relationship, as has been found in TTF-TCNQ.

The salts (TMTSF)₂X show the poorest conductivity along the c axis. In the metallic phase of (TMTSF)₂ClO₄ at low temperatures, the conductivity along the c axis is about 20–25 times smaller than that along the b axis.[18,22] The data on the conductivity and its anisotropy for the (TMTSF)₂X compounds are collected in Table I, with the corresponding characteristics of TTF-TCNQ[7,8,23] and (SN)$_x$[8] given for comparison.

We see from comparing the compounds (TMTSF)₂X and TTF-TCNQ that the anisotropy in the latter is substantially closer to one-dimensional, since the conductivity of TTF-TCNQ in both directions perpendicular to the chains is 100–500 times smaller than the conductivity along the chains. At the same time, in the (TMTSF)₂X class in the metallic phase, the anisotropy has more likely a two-dimensional character, while only the conductivity σ_c is as small as the perpendicular conductivity in TTF-TCNQ. The calculations of the band structure performed by Grant[24] for (TMTSF)₂PF₆ yield the following widths of the conduction band: $W_a \approx 1$ eV, $W_b \approx 500$ K, and $W_c \approx 40$ K. The conclusion regarding the two-dimensional character of the structure in the compounds being studied is confirmed by the data on optical reflection in (TMTSF)₂PF₆. A plasma edge at 25 K was observed by Jacobson et al.[14] for directions of the electric vector E both along the a and the b axis. In the latter case, this amounts to 1/5 of the frequency of a parallel plasmon. In TTF-TCNQ a plasma edge is visible only with a direction of E along the chains.

We note that, if we take into account the symmetry of the complete three-dimensional structure,[25] the electronic band in the (TMTSF)₂X compounds is half-filled, rather than 1/4, as one might conclude from examining a single

TMTSF chain with an equidistant arrangement of the molecules. The splitting of the band of the TMTSF chains into two subbands involves the effect of the potential of the anions, whose period is twice that of the original TMTSF chain. Owing to the action of this potential, the distances between neighboring TMTSF molecules alternate, a gap exists in the center of the one-dimensional band, and the lower subband is half-filled.

b) (BEDT-TTF)X complexes

Crystallographic analysis of specimens with $X = ReO_4$ (Ref. 10) indicates a structure similar to that of (TMTSF)₂X. Figure 2 shows the structure with $X = ReO_4$, while that with $X = I$ is analogous. The transfer of electrons to neighbors in the stack of molecules is carried out by the sulfur atoms. In contrast to the (TMTSF)₂X salts, where the TMTSF molecules are planar, in BEDT-TTF the terminal CH₂ groups lie
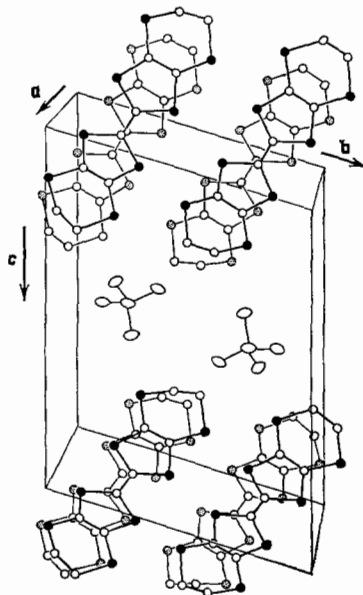

FIG. 2. View of the structure of (BEDT-TTF)₄(ReO₄)₂ along the axis a of the chains.[10] The anions ReO₄ and the molecules BEDT-TTF are shown (the solid and open dots are respectively S and C atoms, while the H atoms are not shown).

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TABLE II.

Cation	X	T_{OD}, K	Q	Type of transition	ΔE, cm⁻¹	P_{OD}, kbar	T_S, K	Type of transition	P_s, kbar	T_c, K	References
(TMTSF)₂	ClO₄—Q	—	—	—			5,5	M-D			34
Ditto	ClO₄—R	24	0,1/2,0	M-M'			—	—	—	1,3	27
" "	PF₆	—					12	M-D	9	1,3	
" "	AsF₆	—					12	M-D	9	1,3	
" "	SbF₆						17	M-D	10,5	0,38	
" "	TaF₆						11	M-D	11	1,35	
" "	FSO₃	87,5	1/2,1/2,1/2	M-D	1100	6				2,1	8
" "	ReO₄	77	1/2,1/2,1/2	M-D	160						27
" "	NO₃	40	1/2,0,0	M-M			12	M-D	8	0,1	
" "	SCN	160	0,1/2,1/2	M-D							27
" "	BrO₄	250	1/2,?,?	M-D							27
" "	H₂F₆	63	1/2,1/2,1/2	M-D							
(BEDT—TTF)₂	ReO₄	81		M-D	1050	6				2	10
Ditto	I									3	11,12

outside the plane of the remaining part of the molecule. Crystals of (BEDT-TTF)X are obtained in the form of plates. Together with the structural data, this indicates that the compounds containing BEDT-TTF molecules are even more similar to quasi-two-dimensional compounds than the (TMTSF)₂X compounds. The measurements of the anisotropy of H_{c2} confirm this conclusion. Actually, in its electronic properties, the (BEDT-TTF)X family belongs to the layer compounds.[26]

3. DIELECTRIC PHASE TRANSITIONS

In almost all compounds of the class being considered, a phase transition is observed at atmospheric pressure upon cooling with complete or partial dielectrization of the electronic system. In the compounds (TMTSF)₂X with the low-symmetry anions X = ReO₄, BF₄, NO₃, and ClO₄, this transition involves ordering of the anions; in crystals containing the octahedral anions PF₆, AsF₆, SbF₆, and TaF₆ ordering of the anions is not found, but there is a transition to a state having a spin density wave (SDW). In both cases the dielectrization of the system arises from the closeness of the electronic spectrum to one-or two-dimensional, and both types of transitions compete with the superconducting transition.

a) Transition with anion ordering

The anions can occupy several orientational positions in the lattice, and a transition from one position to another requires overcoming a potential barrier. At high temperatures the anions are oriented randomly and shift from one position to another by thermal motion. With decreasing temperature they occupy one of the possible positions, since overcoming the potential barrier becomes improbable. The electrostatic energy of the crystal depends on the mutual orientation of the anions, and an order-disorder phase transition in the arrangement of the anions at the point T_{OD} is thermodynamically equivalent to the magnetic ordering of a three-dimensional Ising spin system. The difference of the

anion-ordering transition from the magnetic transition consists only in the fact that anion ordering requires overcoming potential barriers, and the transition occurs rapidly enough only whenever the height of the barriers is not too great in comparison with the temperature T_{OD}. Such potential barriers are absent in magnetic systems. Evidently, an anion-ordering transition has a purely three-dimensional character, and in structural studies it is evident from the appearance of extra reflections from the ordered anion lattice.[25] Table II gives the data for the temperature of the dielectric gap and the wave vectors Q (in units of the reciprocal-lattice vector of the high-temperature phase).[3,27] The transition of the anions into the ordered state substantially affects the electronic system, and this effect has been analyzed in detail by Emery.[28] Owing to the ordering, the anions give rise to an additional periodic potential acting on the electrons. When Q = (1/2, 1/2, 1/2) or (1/2, 0, 0), the wave vector of the periodic potential corresponds to twice the Fermi momentum, since the lower subband is half-filled. Conse-
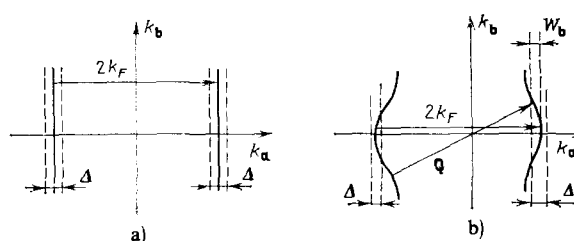

FIG. 3. Fermi surface in the { k_a, k_b } plane in a purely one-dimensional metal (a) and in a metal with anisotropy of one-dimensional type (b). (a) Two regions of the Fermi surface fully coincide with one another upon translation by the wave vector $2k_F$. The potential with the period $2k_F$ gives rise to the gap Δ over the entire Fermi surface, while making the state dielectric. (b) The Fermi surface is curved owing to movement of electrons between chains. The curvature is proportional to the width W_b of the band along the b direction. Under the action of a potential having the wave vector $2k_F$ (along the a axis), a gap Δ arises over part of the Fermi surface if $W_b > \Delta$. More complete dielectrization can occur if the wave vector of the potential has a component $2k_F$ along the a axis and a nonzero component along the b axis (shown by the inclined arrow).

quently a dielectric gap ΔE appears on the Fermi surface corresponding to the direction of momenta along the chain. In this case the influence of the ordering of the anions on the electrons is analogous to the Peierls distortion in the anion lattice (see the reviews of Refs. 23, 29, 30). The transition of the anions to the ordered state is also accompanied by Peierls distortions in the chain of cations and the onset of a charge-density wave (CDW) along the chains. However, it is an essential point that, owing to the three-dimensional character of the electronic spectrum of the compounds being studied, the energy gap that arises from the transition may not cover the entire Fermi surface (Fig. 3). This happens if the amplitude of the potential of the anions and of the CDW V_{2k_F} does not exceed the width of the band of transverse motion of the electrons W_b (along the **b** direction).[31] Therefore the ordering of the anions can lead to complete or partial dielectrization of the electronic system, depending on the ratio V_{2k_F}/W_b. At atmospheric pressure, complete dielectrization is observed in the compound with $X = ReO_4$, and partial in the compound $(TMTSF)_2NO_3$. In the former case the conductivity increases with decreasing temperature above the first-order transition point T_{OD}, while below the point T_{OD} it begins to decline sharply. That is, we are dealing with a metal-dielectric (M-D) transition. In the latter compound, the conductivity sharply declines by a factor of 3–4 with decreasing temperature near the point T_{OD}, while it increases upon cooling throughout the remaining temperature region. That is, a metal-semimetal (M-M') transition occurs. Hereinafter we shall denote by the symbol M' a SDW or CDW state in which the Fermi surface remains partially open. With increasing pressure, the temperature T_{OD} in $(TMTSF)_2ReO_4$ declines rapidly, with $(dT_{OD}/dP) \approx -8$ K/kbar.[32] This can explain the decrease in the difference in electrostatic energy for different orientations of the anions. The amplitude of the periodic potential V_{2k_F} decreases with decreasing T_{OD}. Under the influence of pressure the transition at the point T_{OD} can change in type from dielectric (M-D) to partially dielectric (M-M'). This is just what happens in $(TMTSF)_2ReO_4$ at pressures from 9 to 12 kbar. In this range at the point T_{OD}, only part of the Fermi surface is covered, and upon cooling near the temperature T_{OD}, the resistance sharply increases by about an order of magnitude. It decreases upon further cooling and then one observes a superconducting transition (Fig. 4[32]). Above 12 kbar, ordering of the anions is not observed according to the data on the temperature-dependence of the resistance. Thus, in the range from 9 to 12 kbar, one observes coexistence of the superconducting state and an anion-ordered state. We shall discuss the properties of this phase below in Sec. 6. Now we note only that a situation with coexistence of superconductivity with a CDW phase is found in almost all layered compounds of dichalcogenides of the transition metals (of the type of $NbSe_2$)[26] and in certain trichalcogenides showing anisotropy of one-dimensional type.[33]

Ordering of the anions with different wave vectors **Q** leads to completely different results. In the case **Q** = (0, 1/2, 0) and (0, 0, 1/2), the additional potential of ordering of the anions is the same for all molecules of the cation chain, and
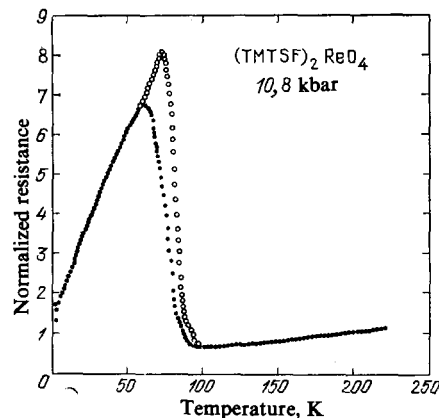

FIG. 4. Temperature-dependence of the resistance along the **a** axis in the compound $(TMTSF)_2ReO_4$ at 10.8 kbar.[32] A transition to the semimetallic state is seen near 80 K, while a superconducting transition occurs at 1.2 K.

the electronic spectrum is altered in the part of the Fermi surface that corresponds to momenta along the **b** axis. This ordering has practically no effect on the temperature-dependence of the resistance. A transition with **Q** = (0, 1/2, 0) is observed in $(TMTSF)_2ClO_4$ upon slow cooling (ClO_4-R).[34] The sharp increase in the intensity of the superstructure peak below $T_{OD} = 24$ K in this compound gives grounds for assuming that the orientational transition belongs to the first-order transitions. Upon fast cooling, the orientation of the anions does not succeed in attaining the equilibrium state. It remains practically random, and the low-temperature properties of the rapidly-cooled compound $(TMTSF)_2ClO_4$-Q turn out to be different. A transition is observed in it below 5.5 K to a spin-density wave (SDW) state.

Upon ordering of the anions with **Q** = (0, 0, 0) or (0, 1/2, 1/2), the additional potential has the same period and phase as the potential of the disordered anions. Hence, after ordering of the anions, the alternation in the chain of cations is enhanced, and it facilitates a transition to the SDW state upon further cooling (see below).

A tendency to dielectrization has also been observed in the orthorhombic phase of the system $(BEDT-TTF)_2I_3$[12]: in a number of specimens the resistance showed a rather sharp peak upon lowering the temperature (Fig. 5). The nature of this dielectric transition is not yet clear. Remarkably, the temperature of the transition to the superconducting state is almost independent of the presence or absence of a dielectric transition. This favors the hypothesis of a multiphase nature of the studied specimens.

b) Transition of the spin-density wave (SDW) type

In the TMTSF compounds with the octahedral ions PF_6, AsF_6, SbF_6, and TaF_6 and in $(TMTSF)_2ClO_4$-Q, ordering of the anions is not observed down to the very lowest temperatures. However, they show a transition to a dielectric or partially dielectric state of the SDW type at a temperature T_s. This same transition is observed in the compound with NO_3 in the part of the Fermi surface that remains open after the transition at the point $T_{OD} \approx 40$ K.

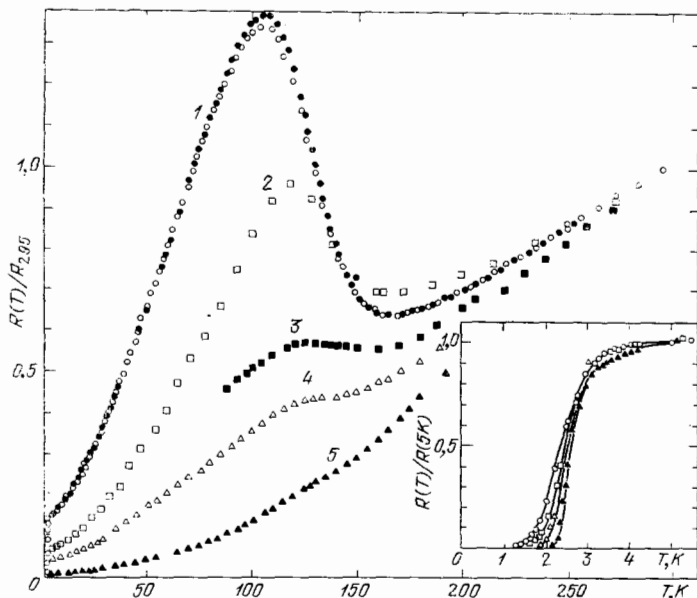FIG. 5. Temperature-dependence of the resistance R for a number of specimens at $(BEDT\text{-}TTF)_2I_3$.[11]

Just as in a Peierls transition, the transition to the SDW state occurs if the Fermi surface contains congruent regions that can be superimposed by parallel translation by the vector $\mathbf{Q}$. In a purely one-dimensional system this superposition is always possible if one takes $\mathbf{Q} = 2k_F$ (see Fig. 3a). Therefore the system of electrons, which is close to one-dimensional in its anisotropy, proves unstable with respect to a dielectric transition of the CDW or SDW type. If the electron-phonon interaction in this situation is strong, a CDW arises. That is, periodic stationary displacements of the molecules with the wave vector $\mathbf{Q}$ appear. They give rise to the periodic potential $V_{\mathbf{Q}}$ for the electrons, and a gap appears proportional to $V_{\mathbf{Q}}$ in the congruent regions of the Fermi surface. If the electron-electron interaction is stronger, the system becomes unstable with respect to a transition to a magnetically-ordered SDW state (Fig. 6). The type of transition (SDW or CDW) is determined by the relation between the electron-phonon interaction parameter $\lambda_{\mathbf{Q}}$ and the magnitude of the Coulomb repulsion $V(\mathbf{Q})$ having the wave vector $\mathbf{Q}$ (for a system close to one-dimensional we have $Q \approx 2k_F$). According to the criterion of Chan and Heine[88] (see also Ref. 89), when $\lambda_{\mathbf{Q}} > V(\mathbf{Q})N(0)$, a CDW instability is manifested. A SDW instability arises when the inequality has the opposite sense. In the SDW state, the peri-
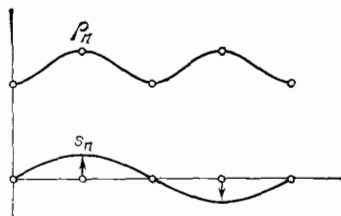
odic effective exchange magnetic field $H_{\mathbf{Q}}$ with the wave vector $\mathbf{Q}$ acts on the electrons. This gives rise to a dielectric gap in the congruent regions of the Fermi surface proportional to $H_{\mathbf{Q}}$. One can observe the SDW transition in magnetic neutron scattering, and it is almost not manifested in x-ray scattering. The difference between the CDW and SDW states is manifested in the magnetic behavior of the system below the transition point: In the case of a CDW the paramagnetism is suppressed, whereas in the SDW system the paramagnetic susceptibility perpendicular to the direction of the magnetic moments remains non-zero at all temperatures, and it is close to the susceptibility observed above the transition point T_s.

In the compounds with $X = PF_6$ and AsF_6, diffuse scattering with the momentum transfer $2k_F$ was not observed upon cooling to the temperature T_s.[35] At the same time the magnetic measurements definitely indicate the onset of a magnetic (antiferromagnetic) structure. This is indicated by the disappearance of the NMR signal from the ^{77}Se nuclei and protons below the temperature T_s owing to line broadening by the internal exchange magnetic field of the electrons.[36–38] The EPR signal also disappears sharply below T_s,[39] and measurements of the temperature-dependence of the magnetic susceptibility indicate behavior characteristic of a SDW transition[40,41] (Fig. 7). Moreover, a resonance in microwave absorption is observed in the compounds with $X = AsF_6$ and ClO_4–Q below T_s that resembles an antiferromagnetic resonance.[42,43]

At atmospheric pressure the SDW transitions in all the compounds of the TMTSF family except $(TMTSF)_2ClO_4$ proved to be metal-dielectric transitions. That is, the conductivity dropped sharply upon cooling below T_s.[3,44,45] The metallic behavior in $(TMTSF)_2ClO_4$–Q was restored in the presence of a strong enough ac electric field[43] and a direct current passed through the crystal.[44] As we have already noted above, a structural transition is absent in $(TMTSF)_2ClO_4$–Q. Precisely in this case one observes a

FIG. 6. Spin-density wave s_n in the $(TMTSF)_2X$ compounds. The onset of the SDW yields three magnetically nonequivalent TMTSF molecules. The spin-density wave also gives to a CDW whose period is half the SDW period. The variation of the electron density ρ_n is shown by the upper curve.
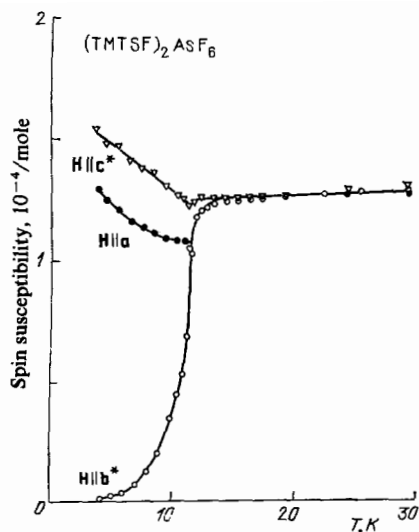
FIG. 7. Temperature-dependence of the paramagnetic susceptibility for various directions of the magnetic field in $(TMTSF)_2AsF_6$.[40]

SDW transition. The situation in the R-phase is different: the orientational transition at 24 K leads to the absence of any signs of SDWs down to the temperature of the supercon-ducting transition with $T_c \approx 1.3$ K.[38]

One can depress the metal-SDW transitions by apply-ing pressure, which apparently enhances the deviations of the electronic spectrum from one-dimensional type, and thus decreases the SDW transition temperature. Above the critical pressure P_s, the SDW transition disappears in all the $(TMTSF)_2X$ compounds and, apart from $X = NO_3$, they all go over into the superconducting state (see Table II). Figure 8 shows a typical behavior of the conductivity as a function of the temperature for $P < P_s$ and $P > P_s$ in $(TMTSF)_2AsF_6$.[3] Figure 9 shows the phase diagram for this compound in the (T, P) plane.[49] The region is cross-hatched in Fig. 9 where one should observe coexistence of SDWs and superconduc-tivity. There are as yet no reliable data confirming the exis-tence of such a region in the compounds with octahedral ions, but the theory predicts that this region must exist. We
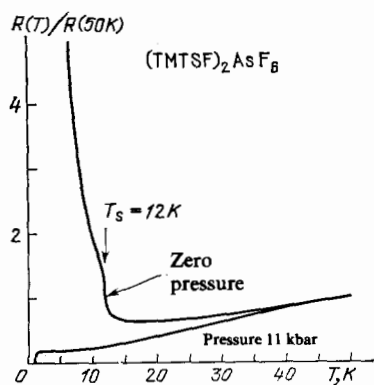

FIG. 8. Temperature-dependence of the longitudinal resistance in $(TMTSF)_2AsF_6$ below 50 K.[30] At atmospheric pressure we see a metal-dielectric transition at $T_s \approx 12$ K. At 11 kbar pressure the metallic state persists upon cooling, and a superconducting transition occurs at the point $T_c \approx 1.1$ K.
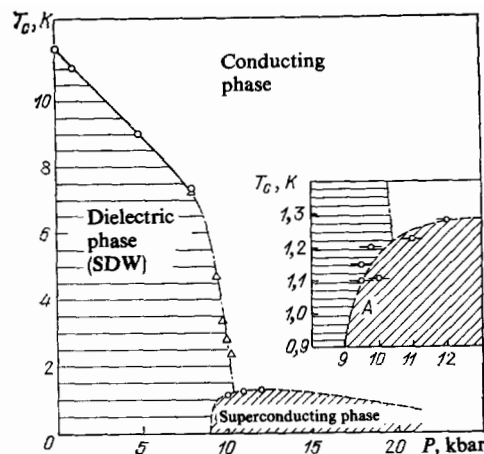

FIG. 9. Phase diagram of $(TMTSF)_2AsF_6$ in the (P, T) plane according to the data of Ref. 49. A—region where superconductivity and a SDW coex-ist.

see from Fig. 9 that the superconducting critical tempera-ture T_c declines rapidly with increasing pressure above P_s.

We must note that a transition of the SDW type has as yet been found in the family of quasi-one-dimensional com-pounds only in crystals containing the molecule TMTSF, while a CDW transition is observed in all the remaining cases. A possible reason why a SDW instability is observed in TMTSF chains is discussed below.

We have already noted previously that pressure wea-kens the instability of the metallic system with respect to SDW transitions. These facts led Bechgaard to the remarka-ble idea of replacing the octahedral ion AsF_6 with the tetra-hedral ion ClO_4 having smaller dimensions. As a result this "chemical compression" acts analogously to pressure, and thus the first organic superconductor at atmospheric pres-sure was obtained: $(TMTSF)_2ClO_4$.[2] The equivalence of pressure and "chemical compression" along the c axis is demonstrated in Fig. 10, where we see that P_s declines mon-otonically with decreasing lattice parameter c.[3] Wudl[16] not-ed (see also Ref. 86) that the "chemical compression" in re-placing AsF_6 with the smaller anion PF_6 leads to equalization of the lengths of the S–S bonds along the a and b axes. That is, the electronic spectrum becomes more two-dimensional with decreasing dimensions of the anion. The equivalence of the action of "chemical compression" and pressure on T_s allows us to suppose that pressure also makes
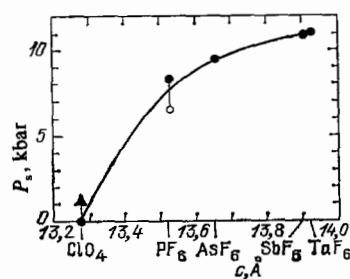

FIG. 10. Dependence of the critical pressure P_s on the room-temperature lattice parameter c.[3]

the spectrum of the electrons approach the two-dimensional type.

4. ELECTRIC AND MAGNETIC PROPERTIES OF THE SDW PHASE

Now we shall examine the properties of the SDW phase in the dielectric and semimetallic nonsuperconducting states (above T_c).

In the magnetically ordered SDW state, each TMTSF molecule has a nonzero spin density whose distribution is characterized by the wave vector $Q = 2k_F$. If we do not as yet take into account the weak effect of the potential of the anions and the dimension of the chain of cations caused by it, then the wave vector $2k_F$ corresponds to a quadrupling of the period of the equidistant chain of TMTSF molecules, and the spin density of the SDW phase is described by the expression

$$s_z(n) = s \cos \left(\frac{\pi}{2} n + \varphi \right). \tag{2}$$

Here n is the number of the molecule and φ is the SDW phase. The spin-density wave of (2) gives rise to an effective exchange field that varies with n according to the same law, and this field gives rise to the dielectric gap $\Delta_s \sim s$ at the Fermi surface. Therefore the SDW and CDW phases prove equivalent from the standpoint of the behavior of the conductivity. They are also quite equivalent in their thermodynamic properties in the absence of external fields. However, the mechanisms that fix the phase φ of the wave differ somewhat for SDWs and CDWs. In a Peierls transition the charge-density wave, in the first order with respect to its amplitude, interacts with the original crystal lattice or with charged impurities. This is impossible for an SDW, but in second-order perturbation theory with respect to its amplitude it gives rise to a CDW. The latter can now be pinned by the lattice or by charged impurities.[81] The amplitude of the CDW that accompanies the SDW is proportional to $(T_s / W_a)^2$. It is small, and the pinning proves weaker than in the case of a CDW transition. Now let us recall the potential of the anions and the dimerization of the chain of cations caused thereby. Evidently it leads to pinning of the SDW, since its period coincides exactly with the period of the induced CDW. The energy of commensurability is $\varepsilon_c \approx V_a (\Delta_s / W_a)^2 \cos 2\varphi$, where V_a is the effective potential of the anions and of dimerization of the cation chain. The system attains minimum energy when $\varphi = 0$ or $\pi/2$. In either case the spin density on a molecule takes on the values $\pm s$ and 0, depending on its number, as shown in Fig. 6. The changes in the electron density along the chain are shown in the same place. We see that the spin density changes sign in going from one unit cell (2 molecules of TMTSF!) to another. That is, we are dealing with an antiferromagnetic transition. However, the spin density is distributed very inhomogeneously within the unit cell: 0 on the one molecule, and almost 0 (more exactly, sV_a / W_a) on the other molecule. We note that the value of s in the SDW state is small. It is proportional to Δ_s / W_a, and according to the estimates,[42,43] it amounts to from 10% to 20% of the nominal value 1/2.

Just like the CDW phase, the SDW state has an optical-

ly active Fröhlich collective mode, and the dielectric permittivity of the compounds $(TMTSF)_2X$ in the SDW state must be large (of the order of W_a / V_a). As applied to organic superconductors, the problem of the contribution of the Fröhlich collective mode to the conductivity has been discussed by Fenton.[90]

In addition to the single-particle excitations and the Fröhlich collective mode (oscillations of the SDW phase), the SDW state also has a collective oscillation involving rotation of the spins. It corresponds to a spin wave of magnetically ordered crystals. In a system without anisotropy the spectrum of this excitation has the form $\omega \sim V_F k$ or $W_a (ka)$, where a is the distance between TMTSF molecules in the chain. The sonic character of this spectrum is a consequence of the Goldstone theorem (the SDW state is degenerate with respect to the direction of the spin in space, i.e., in Eq. (1) we can take s_x or s_y instead of s_z). In the presence of magnetic anisotropy,[47] as $k \to 0$, we obtain the value $\omega(0) \approx \sqrt{W_a D}$, where D is the anisotropy parameter. This mode of oscillations corresponds to antiferromagnetic resonance in magnetic materials having localized moments. It has been observed in compounds with $X = PF_6$ by Torrance et al.,[42] and with $X = ClO_4$ by Walsh et al.[43]

Great interest is aroused by the behavior of the magnetoresistance in the SDW phase of the compounds $(TMTSF)_2X$. A detailed study of this problem is contained in the review by Gor'kov[48] (on the influence of a magnetic field on the transition to the SDW phase, see also Ref. 82).

5. SUPERCONDUCTING PROPERTIES

Detailed information has been collected up to the present on the thermodynamics of the superconducting transition in $(TMTSF)_2ClO_4$ and the anisotropy of the upper critical field in the compounds with $X = ClO_4$, PF_6,[18,46] and AsF_6,[48,49] and in $(BEDT-TTF)X$ (see Table I).[11,12] They all indicate that the superconducting properties of this family of superconductors is well described within the framework of the Bardeen-Cooper-Schrieffer (BCS) model.

In $(TMTSF)_2ClO_4$ one observes a rather sharp jump in the heat capacity at the point T_c [15] (Fig. 11). Here the ratio of the jump ΔC to the electronic heat capacity $C_e(T)$ is 1.67,
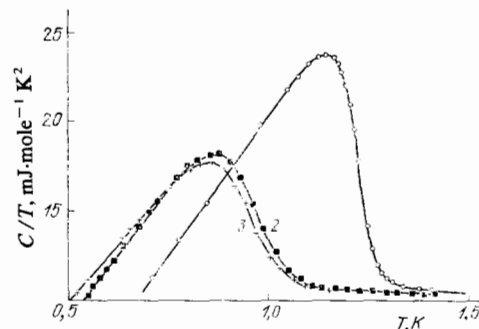
FIG. 11. Temperature-dependence of the electronic component of the specific heat in $(TMTSF)_2ClO_4$-R in the region of the superconducting transition.[15] 1—after slow cooling (R-phase); 2—after fast cooling from 70 K (Q-phase); 3—after fast cooling from 40 K.
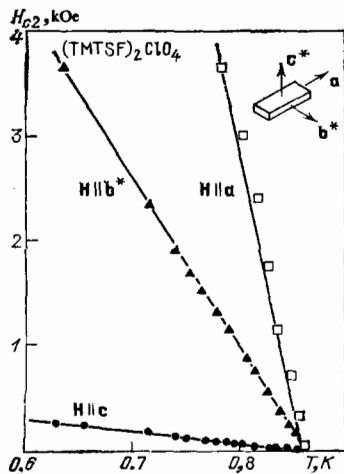
FIG. 12. Temperature-dependence of the upper critical field in $(TMTSF)_2ClO_4$ along the directions **a**, **b***, and **c**.[18]

which is somewhat larger than the corresponding value 1.43 in the BCS theory. An estimate of the energy of the superconducting condensation

$$\int_0^{T_c} (C_{es} - C_e) \, dT$$

yields the thermodynamic critical field $H_0 \approx 44$ Oe, with a magnitude of the gap $\Delta_0 \approx 2$ K at $T = 0$ ($T_c = 1.2$ K), in good agreement with the corresponding relationship in the BCS theory ($\Delta / T_c = 1.76$).

The data on the anisotropy of the upper critical fields[18] presented in Table I agree with the results of measuring the anisotropy of the conductivity in the normal state at low temperatures. Figure 12 shows the $H_{c2}(T)$ relationship in $(TMTSF)_2ClO_4$ along the three directions **a**, **b**, and **c**.[18] Just like the conductivity, the character of the anisotropy of H_{c2} does not allow us to speak of a quasi-one-dimensional character, but of a quasi-two-dimensional character of the superconductivity in this compound. In the case of (BEDT-

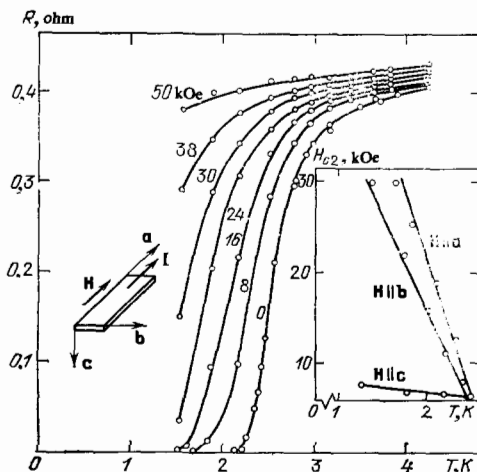FIG. 13. Curves of the transition to the superconducting state of (BEDT-TTF)$_2$I$_3$ in a magnetic field oriented along the **a** axis.[11] The inset shows the temperature-dependence of the critical fields along the **a**, **b**, and **c** axes.

TTF)$_2$I$_3$, anisotropy in the **a**,**b** plane now is practically completely absent (Fig. 13; here the **b** axis corresponds to the direction along the chains).[11] We can check whether relationships are fulfilled between the conductivity, the upper critical magnetic field near T_c, and the linear coefficient γ in the heat capacity that are characteristic of impure superconductors of the second kind with a mean free path $l \ll \xi_0$. Here ξ_0 is the superconducting correlation length at $T = 0$, which is equal to $\hbar v_F / \pi \Delta_0$. These relationships for an anisotropic superconductor have the form (see Ref. 50):

$$H_a' = \left(\frac{dH_{c2a}}{dT}\right)_{T_c} = \frac{1,9k_B\Phi_0}{\hbar \sqrt{D_b D_c}},$$

$$H_i' = \left(\frac{dH_{c2i}}{dT}\right)_{T_c}, \qquad \Phi_0 = \frac{\pi \hbar c}{e}, \tag{3a}$$

$$\frac{H_b' H_c'}{H_a'} = \frac{1,9k_B\Phi_0}{\hbar D_a} = \frac{1,9\Phi_0 k_B 2e^2 N(0)}{\hbar \sigma_a}, \qquad \sigma_a = 2e^2 D_a N(0). \tag{3b}$$

The density of states can be determined from the specific heat data.[15] The values of H_i' are given in Table I. Upon substituting the values $\sigma_a \approx 10^5$–10^6 ohm^{-1} cm^{-1} for $(TMTSF)_2ClO_4$ crystals,[17] we obtain 0.5–0.05 kOe/K for the right-hand side of the first relationship of (3b), while the left-hand side equals 0.37 kOe according to the data of Ref. 18 (the conductivity σ_a for the crystals of $(TMTSF)_2ClO_4$ studied in Ref. 18 is unknown, but it lies in the range 10^5–10^6 ohm^{-1} cm^{-1}). Thus the magnitude of the upper critical magnetic field near T_c agrees with the results of the BCS theory for an impure superconductor.

The upper critical field parallel to the chains in $(TMTSF)_2ClO_4$ at low temperatures proves to be very large, reaching magnitudes of 11 kOe at 0.55 K.[18] Evidently the breakdown of superconductivity for this field direction at low temperatures is mainly determined by the paramagnetic effect,[50] and the Clogston paramagnetic limit amounts to 11.8 kOe at 0.55 K, in agreement with the experimental data.[18] The situation in (BEDT-TTF)$_2$I$_3$ for a field along the (**a**,**b**) layers is analogous (see Fig. 13).

Thus we see that the BGS self-consistent-field theory describes well the supeconducting properties of the $(TMTSF)_2X$ compounds at all temperatures. We can conclude from all that we have said that the experimental data do not indicate the presence of any strong one-dimensional superconducting fluctuations in the compounds under study.

At the same time, a number of studies (see Refs. 23 and 51) have discussed the possibility of interpreting the experimental data for the $(TMTSF)_2X$ superconductors within the framework of a model of quasi-one-dimensional superconductors, or in other words, a model with Josephson interaction of the chains. It is assumed in this model that the condition $\hbar \tau_\perp \ll T_{co}$ is satisfied, where $\tau_\perp$ is the time for hopping of the electron between chains (in the model of diffusional motion we have $\tau_\perp^{-1} = d^2/D_\perp$, where d is the distance between chains). Further, T_{co} is the critical temperature of the superconducting transition in a chain in the self-consistent-field approximation. Since in a one-dimensional system the fluctuations destroy the long-range superconducting order, the

three-dimensional order in a quasi-one-dimensional super-conductor arises only because of the transitions of the electrons between chains, and its temperature $T_c \to 0$ as $\tau_\perp^{-1} \to 0$. That is, we have $T_c = T_{co}(\tau_\perp T_{co})^{-\gamma}$, where $\gamma > 0$. Here one must observe strong superconducting fluctuations above T_c up to temperatures of the order of T_{co}, and they should be visible in measurements of the specific heat. The absence of any anomalies in the specific heat above T_c in $(TMTSF)_2ClO_4$[15] does not confirm the model of a Josephson interaction of the chains. Moreover, the behavior of H_{c2} also allows one unambiguously to distinguish quasi-one-dimensional behavior $(\hbar/\tau_\perp \ll T_{co})$ from two- or three-dimensional. According to theoretical calculations,[52,53] in the quasi-one-dimensional model below some temperature $T^* \lesssim T_c$, the critical field parallel to the chains must increase sharply.

For a field parallel to the chains, an orbital effect of the field below T^* is completely absent, and for this direction we have $H_{c2} \approx T_{co}/\mu_B$. When we take fluctuational effects into account,[83] a field perpendicular to the chains breaks down the superconductivity also owing to the orbital effect. However, the corresponding critical field far exceeds the magnitude obtained by extrapolating the $H_{c2}(T)$ relationship near T_c into the low-temperature region. Evidently the experimental data do not fit this situation, since in the studied superconductors the field perpendicular to the a,b plane is determined by the orbital effect, and the value of H_{c2} at low temperatures agrees with the magnitude of the derivative $(dH_{c2}/dT)_{T_c}$, namely $H_{c2}(0) \approx 0.7\, T_c\, (dH_{c2}/dT)_{T_c}$. At the same time, the critical field along the a axis in $(TMTSF)_2X$ and along the a,b plane in $(BEDT-TTF)_2I_3$ reaches the paramagnetic limit H_p determined by the temperature T_c.

We note that the data on magnetoresistance at temperatures $T_c < T < T_{co} \approx 20$ K have been interpreted within the framework of concepts of strong fluctuations above T_c in $(TMTSF)_2X$. However, it was shown in Ref. 54 that these results can be explained also within the framework of ordinary band theory (for more details, see the review by Gor'kov[48]). As another argument favoring fluctuational one-dimensional superconductivity, data have been used from tunneling experiments (the characteristics of the Schottky barriers formed by a single crystal of $(TMTSF)_2PF_6$ sputtered with the n-type semiconductor GaSb were studied at a pressure $P \approx 11$ kbar[55]). From an analysis of the characteristics of the contacts, More et al.[55] concluded that a pseudogap in the density of states appeared below 15 K. Analogous results were obtained also at $(TMTSF)_2ClO_4$–GaSb contacts.[55] The complexity of the experiments and of the interpretation of the characteristics does not allow one to decide unequivocally on the basis of these data concerning the existence of a superconducting pseudogap in the density of states. Moreover, later studies of $(TMTSF)_2ClO_4$–Al_2O_3–Au contacts[56] indicate the existence of a substantially smaller gap corresponding to the value $T_c \approx 2$–6 K. This is rather close to the observed transition temperature. Now experimental data have appeared that indicate a connection between the anomalies in the tunneling characteristics and anion ordering (see the review by Gor'kov[48]). Thus there are no convincing data at present on a one-dimensional regime

of superconductivity in $(TMTSF)_2X$. On the contrary, everything indicates the applicability of the ordinary BCS theory for describing the superconducting transition in organic superconductors. Arguments for and against the existence of superconducting fluctuations at temperatures substantially above T_c have been presented in the studies of Schulz et al.[92] and of Kwak.[93]

Now let us discuss the problem of to what extent do organic superconductors resemble quasi-two-dimensional systems. A Josephson interaction of the layers is realized if the time for hopping of the electrons between layers $\tau_\perp$ satisfies the condition $r = h/\tau_\perp T_c \ll 1$.[26,57] The time $\tau_\perp$ is determined by the diffusion coefficient D_c and the distance d between the layers. Upon expressing D_c in terms of $H'_\perp$ by using Eq. (3), we obtain the following expression for the parameter r that characterizes the dimensionality of the superconductivity:

$$r_c = \frac{8\Phi_0 H_c}{\pi d^2 T_c H'_a H'_b}. \tag{4}$$

This parameter attains its smallest value in $(BEDT-TTF)_2I_3$, but even here it amounts to about 4. Thus, as yet a Josephson regime has not been realized in organic superconductors, and we are dealing with the ordinary anisotropy of three-dimensional superconductivity. We note that a larger degree of two-dimensional anisotropy is attained in layered intercalated compounds. Thus, $r \approx 0.5$–1 has been obtained in the system 2H-TaS$_2$ (pyridine)$_{1/2}$.[58]

Quasi-two-dimensional superconductors (with $r_c \ll 1$) are characterized by a sharp growth in the critical field parallel to the layers as the temperature approaches the point $T^* = (1$–2$)\cdot T_c$. Near and below T^*, the magnitude of H_{c2} for superconductivity along the layers is determined here only by the paramagnetic limit, and as $T \to 0$, we obtain $H_{c2} \approx 15.5\, T_c$, where H_{c2} is expressed in kOe, and T_c in K. Superconducting currents between the layers below T^* are destroyed by a parallel magnetic field owing to fluctuational effects. Corresponding estimates of the critical field $H_{c2\parallel}$ have been given by Efetov.[83] Moreover, Josephson oscillations of the current should be observed in an electric field perpendicular to the layers. These effects have not yet been observed, since the regime $r \ll 1$ has not been reached. However, it is not ruled out that organic compounds will prove more suitable for obtaining Josephson interaction of the layers than the layered intercalated compounds. Apparently the crystal structure of the organic compounds is more nearly perfect than that of the intercalated compounds, and it is easier to avoid short-circuiting of the layers in them.

In closing this section we shall take up the role of structural defects and impurities in organic superconductors. In ordinary metals nonmagnetic impurities do not affect the value of T_c. However, in the organic compounds the breakdown of the crystal structure and of the conjugation chains in the molecule give rise to unpaired spins—free radicals. The presence of these spins yields a Curie law that depends on the paramagnetic susceptibility at low temperatures. An increase in the susceptibility at low temperatures associated with this effect has been observed in practically all quasi-one-dimensional organic compounds.
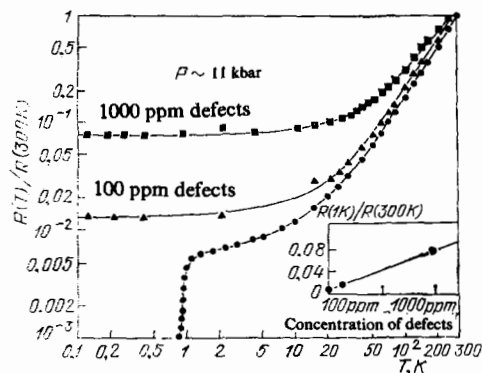
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FIG. 14. Temperature-dependence of the resistance at 11 kbar pressure after irradiation of $(TMTSF)_2PF_6$ crystals.[18]

It was noted in Ref. 52 that unpaired spins act on the singlet superconductiviy as magnetic impurities.[59] They decrease the temperature of the superconducting transition at low concentrations and completely suppress it when their concentration exceeds a critical value. Thus the role of defects in organic superconductors can be large, whereas in ordinary metallic superconductors defects do not affect T_c. Experimental studies confirm this conclusion. The suppression of superconductivity by defects arising upon irradiating $(TMTSF)_2PF_6$ with protons and x-rays has been studied.[18] The influence of defects on the resistance is shown in Fig. 14,[18] from which we see that a concentration of defects of 100 ppm completely suppresses the superconducting transition.

According to the data of Ref. 18, the relation of T_c to the concentration x of unpaired spins is characterized by the quantity $dT_c/dx \approx 60$–100 K/at.%. According to the Abrikosov-Gor'kov theory,[59] this value of dT_c/dx corresponds to an exchange interaction of the unpaired spin and the conduction electrons with an exchange integral $J \approx 0.5$ eV. Most likely the unpaired spins lie inside the chain of cations in TMTSF molecules transformed by the irradiation, since the estimate obtained for J coincides with the energy scale of the Coulomb repulsion of electrons inside a TMTSF molecule.

Another explanation of the strong dependence of T_c on the defects in irradiated organic compounds has been proposed by Abrikosov.[95] It assumes that a p-type triplet pairing is realized in organic superconductors, and this is suppressed strongly by ordinary impurities.[96] However, this hypothesis faces difficulties in interpreting the experimental data for the upper critical magnetic field H_{c2}. In the case of triplet pairing, the paramagnetic limit does not exist, whereas the magnitude of H_{c2} along the axis of maximum conductivity in $(TMTSF)_2ClO_4$ and $(BEDT-TTF)_2I_3$ is restricted precisely by the paramagnetic limit.

6. COMPETITION AND COEXISTENCE OF THE SUPERCONDUCTING STATE AND THE SDW (OR CDW) STATE

First we shall discuss the question as to what type of theory is applicable for describing phase transitions in the compounds being studied: a theory reflecting the specifics of one-dimensional systems, or the ordinary self-consistent-field theory used for describing three-dimensional systems (see Ref. 26).

The theories describing one-dimensional metals begin with the study of Bychkov, Gor'kov, and Dzyaloshinskiĭ.[60] They take into account the fact that the Cooper pairing of electrons in a one-dimensional system interacts with the electron-hole pairing that gives rise to CDWs and SDWs, and both these types of pairing enhance one another. Therefore, in determining the ground state in a one-dimensional system of electrons, all types of pairing must be taken into account simultaneously, even when one adopts frameworks that go outside the limits of self-consistent-field theory. The form of the ground state depends on the parameters g_1 and g_2 that describe the interaction of electrons having the momentum transfer $2k_F$ and zero, respectively. In the case $g_1 > 2g_2$ superconducting instability predominates, and dielectric instability (CDW or SDW) predominates when $g_1 < 2g_2$.[61] Taking into account interactions between the chains in the quasi-one-dimensional crystal makes possible a real phase transition with three-dimensional ordering of the superconducting or dielectric type (see Refs. 62–64). In the case of predominant superconducting instability, the temperature T_c of the three-dimensional transition increases at first with increase in the transverse resonance integral $t_\perp$. It reaches a maximum when $t_\perp \sim \Delta$ (Δ is the superconducting order parameter in a single chain at $T = 0$ in the self-consistent-field approximation). Then it declines with further increase in $t_\perp$, since in the limit as $t_\perp \gg \Delta$, all the specific one-dimensional effects drop out, and the electron-hole instability no longer enhances, but weakens the superconducting instability.[65,66] We have noted above that the experimental data and calculations of the band structure in organic superconductors do not agree with the picture of quasi-one-dimensional behavior. Therefore, one can use the ordinary self-consistent-field theory for describing the competition of the superconducting transition with dielectric transitions of the CDW or SDW types.

Bilbro and MacMillan have constructed a theory that takes into account the competition and the possibility of coexistence of superconducting and electron-hole pairing of the CDW type.[67] It has been successfully applied to explain the experimental data in systems of the A-15 type and in other compounds where a CDW transition of the M-M' type is observed with a subsequent superconducting transition (see Ref. 68). Machida and Matsubara[69,70] and Yamaji[91] have extended the theory of Ref. 67 to systems having a SDW transition instead of a CDW transition. The models examined in Refs. 67 and 69 are equivalent in their thermodynamic properties in the absence of an external field.

A model of the Fermi surface has been studied in Refs. 67 and 69 that contains congruent or almost congruent regions in one of its parts (the density of states of this part is $N_1(0)$). The congruent regions facilitate the appearance of a CDW or SDW, depending on the relationship between the electron-phonon and exchange interactions of the electrons. Transitions of this type lead to covering of part of the Fermi surface with a dielectric gap. These transitions compete with the superconducting transition, which is accompanied by

appearance of an additional supeconducting gap over the entire Fermi surface. The models of Refs. 67 and 69 permit only competition of transitions, and the temperatures T_s and T_c can only be decreased by the mutual influence of the transitions, in contrast to the quasi-one-dimensional situation.

Analysis of the models has shown that two types of behavior can occur, depending on the parameter $\rho = N_1(0)/N(0)$. With a large enough value of ρ, a dielectric transition first occurs to a semimetallic phase, and then superconducting pairing occurs in the CDW (or SDW) phase at the temperature T_c, which is determined by the relationship

$$T_c^{1-\rho} T_s^{\rho} = T_{c0}. \qquad (5)$$

Here T_{c0} is the temperature of the superconducting transition in the absence of the CDW or SDW transition. When $\rho = 1$, the entire Fermi surface is covered by a dielectric gap, and a superconducting transition becomes impossible. When the value of ρ is small, only a superconducting transition is realized at the temperature T_{c0}. According to the ideas presented above, in the case of a SDW transition the parameter ρ declines upon applying pressure, since the increase in the transverse resonance integral diminishes the congruent regions of the Fermi surface, and correspondingly diminishes the values of $N_1(0)$ and ρ. In the case of an anion-ordering transition, the effect of pressure also reduces to decreasing the parameter ρ in Eq. (5), although the parameter T_s no longer has the meaning of the anion-ordering temperature, since the thermodynamics of this transition is not described by the model of Ref. 67. If we take into account the fact that the temperature T_{c0} decreases with increasing pressure, then the resulting phase diagram in the (P, T) plane coincides with that shown in Fig. 9. The diagram always contains a region of coexistence of an SDW and superconductivity, although it may have a very narrow range of pressure. In the region from P_c to P_s, on cooling the compound must first transform to the SDW state, since an increased resistance must be observed below the transition point T_s. Then the superconducting transition occurs at the point T_c, whereupon the resistance vanishes. Behavior of this type has been found in many specimens of $(TMTSF)_2X$, e.g., with $X = PF_6$ in the pressure region from 9 to 11 kbar[49] and in $(TMTSF)_2ClO_4$–Q without pressure (see also Refs. 71 and 72). However, in all these cases, one must not rule out the possibility that a normal phase exists in part of the specimen owing to its inhomogeneity. This phase then transforms to the superconducting phase, while the other part remains in the dielectric phase down to the lowest temperatures. Schwenk et al.[94] note that the experimental data for specimens of $(TMTSF)_2ClO_4$ studied under various regimes of cooling and annealing agree with the assumption that the specimen is divided into superconducting and dielectric (SDW) regions.

We note that the model of Refs. 69 and 70 does not take into account another mechanism of interaction between superconductivity and magnetism—the effect of the exchange field I of the magnetic moments of the SDW on the conduction electrons (see Ref. 90). Owing to the antiferromagnetic type of order of the moments, the destructive action of this field is described by the energy parameter $\tau_m^{-1} = I^2 N(0)$.[47]

If it is small in comparison with T_c, then we can neglect this mechanism of exchange magnetic biassing of the electrons.

Approximately the same kind of parameter also describes the exchange scattering of electrons by the spin excitation of the SDW phase. Since $I = I_0 s$, the parameter τ_m^{-1} is small in proportion to the smallness of the square of the exchange interaction of the electrons I_0^2 and the amplitudes s^2 of the SDW wave. The parameter I_0 determines the exchange enhancement of the paramagnetic susceptibility χ_p of the electrons according to the relationship $\chi_p \sim N(0)[1 - I_0 N(0)]^{-1}$. In principle, one can estimate it from the experimental data, which allow one to determine χ_p and $N(0)$ independently. As yet the information needed for this does not exist, since the electron-phonon interaction parameter λ is not known (knowing it would make it possible to find $N(0)$ from the relationship $\gamma \sim N(0)(1 + \lambda)$.

We note that the possible coexistence of electron SDWs and superconductivity is not a unique property inherent only in organic compounds. The coexistence of superconductivity and magnetism of collectivized electrons (SDW) has been found in the compound Y_9Co_3,[73] which has $T_s \approx 6$ K and $T_c \approx 3$ K, in the alloys $Cr_{1-x} Re_x$ with $T_s \approx 160$ K and $T_c \approx 3.5$ K,[74] and in the compounds $YbRh_2Si_2$ and $LuRh_2Si_2$ with $T_s \approx 50$ K and $T_c \approx 4$ K.[75] These compounds possess a small anisotropy, and the SDW transitions in them do not affect the electronic conductivity. In the $(TMTSF)_2X$ family, which has a rather strong anisotropy, the mechanism of interaction of the SDW with the superconductivity mainly reduces to competition in the "struggle" for the Fermi surface. This distinguishes them from the above-listed compounds of the transition elements. There is as yet no consistent theory of the coexistence of superconductivity and band magnetism that takes into account all aspects of their interaction. This is explained by the fact that both the SDW transition and its interaction with superconductivity are substantially determined by the geometry of the Fermi surface, and the construction of a quantitative microscopic theory is impossible without an exact knowledge of the electronic band structure of the crystal.

7. PROSPECTS FOR INCREASING THE CRITICAL TEMPERATURE IN ORGANIC SUPERCONDUCTORS

It is evident from the treatment above that superconductivity is suppressed in all the $(TMTSF)_2X$ compounds except $X = ClO_4$–R, either by transition to an SDW (or CDW) state according to Eq. (3), or by the pressure, which eliminates the dielectric transition, but per se lowers the value of $T_{c0}(P)$. We can estimate $T_{c0}(P)$ for $P \to 0$ from the data for $(TMTSF)_2PF_6$ by assuming that the SDW transition is completely suppressed above P_s, and the $T_c(P)$ relationship here coincides with $T_{c0}(P)$. Upon adopting the experimental value $(d T_c/d P)_{P = P_s} \approx -(0.06–0.09)$ K/kbar, we obtain the extrapolated value $T_{c0}(0) \approx 2$–3 K. This value characterizes the potentialities of the electron-phonon interaction in $(TMTSF)_2PF_6$. The value of $T_c(P_s)$ proves to be the same in all compounds with symmetric anions that lie to the right of ClO_4 in Fig. 10. This implies that chemical compression depresses T_{c0} in the same way as pressure does. The equiv-

alence of the action of pressure and chemical compression implies that the value of T_{c0} ($p = 0$) declines with decreasing c. We can explain this decline by the decrease in electron-phonon interaction upon compressing the system, owing to an increase in the phonon frequencies. This behavior of the electron-phonon interaction parameter λ and T_c upon compression and the concomitant hardening of the phonons is characteristic of most superconductors. We see that the organic superconductors constitute no exception (see Chap. 4 in Ref. 5). This tendency makes it possible to understand the difference in behavior of TTF-TCNQ and the $(TMTSF)_2X$ compounds. The latter are more three-dimensional, and the role of the electron-pronon interaction in them proves to be smaller than the role of the Coulomb interaction. We can see this from the fact that SDW instability is manifested, rather than Peierls instability. At the same time, in TTF-TCNQ the electron-phonon interaction leads to Peierls instability with a rather high transition temperature T_P. We can suppose that this difference mainly involves the difference in the electron-phonon, rather than the Coulomb interaction parameter in these systems. Actually, the system of phonons in TTF-TCNQ proves to be softer than in the $(TMTSF)_2X$ compounds. This is directly indicated by a comparison of the Debye temperatures in $(TMTSF)_2ClO_4$ ($\theta_D \approx 213$ K[15]) and in TTF-TCNQ ($\theta_D \approx 89.5$ K[76]).

The greater value of θ_D in the $(TMTSF)_2X$ compounds can be explained by the approach of the positive charges of the holes in the chain of cations, which are situated mainly on the Se atoms, to the negative charges of the anions with the approach being the closer the smaller is the anion. At the same time, the rather uniform distribution of positive charge within the TTF molecules leads to a reduction of the electrostatic interaction of the charges[16] and a corresponding softening of the lattice. The magnitudes of the phonon frequencies involve the dimensionless electron-phonon interaction parameter λ_Q via the relationship

$$\lambda_Q = \frac{N(0)\, I_Q^2}{M\omega_Q^2}. \tag{6}$$

Here $N(0)$ is the density of states per TMTSF molecule, M is the mass of the cations, and ω_Q is the phonon frequency. The matrix element I_Q contains a contribution from the intermolecular vibrations (it is proportional to the derivative of the resonance integral with respect to the distance between the molecules along the chains) and a contribution from the intramolecular vibrations that depends on the structure of the molecules. For TTF-TCNQ these contributions are of the same order of magnitude (see Chap. 7 of Ref. 5). In going from TTF-TCNQ to the $(TMTSF)_2X$ compounds, the magnitude of $\omega_Q^2 \sim \theta_D^2$ increases by a factor of four, the value of M varies insignificantly, and we can suppose that the variation in the matrix element I_Q is not so large as the variation of ω_Q. Consequently λ_Q decreases, the difference $\lambda_Q - V(Q)N(0)$ becomes negative, and an SDW type of instability is observed in the $(TMTSF)_2X$ compounds, rather than CDW.

Thus TTF-TCNQ crystals prove to be rather soft in the phonon sense owing to their one-dimensionality. The parameter λ in them is large, but precisely because of the strong one-dimensionality of the electronic spectrum one observes a dielectric Peierls transition in them, rather than a transition to the superconducting state.

In going to the $(TMTSF)_2X$ compounds, we have obtained a more compact system (two-dimensional), but one more rigid with a smaller parameter λ. Under conditions in which the anisotropy of the electronic spectrum is close to one- or two-dimensional, while the electron-phonon interaction is weakened in comparison with the Coulomb interaction, the $(TMTSF)_2X$ compounds manifest a tendency to weak dielectrization of the SDW type. The temperatures of the SDW transition prove to be rather low, but yet they exceed the value $T_{c0} \approx 2$–3 K. Suppression of the SDW by chemical or mechanical compression yields an additional lowering of the parameter λ, and consequently T_c decreases to values of 1–1.3 K.

As yet little is known concerning the change in properties of the $(BEDT-TTF)X$ salts on changing the anion X, but we can suppose that the transition from ReO_4 to I also leads to chemical compression and elimination of the dielectric transition. The value of the derivative $(d\,T_c/d\,P)_{P_{OD}} = -0.3$ K/kbar implies that $T_{c0} \approx 4$ K.

The ideas that we have presented on the role of phonon softening in determining T_c can be tested by measuring the specific heat in a number of $(TMTSF)_2X$ compounds. These measurements enable one to find $N(0)$ and θ_D as functions of the identity of X above T_s. According to MacMillan[77] (see Chap. 4 of Ref. 5), the electron-phonon interaction parameter λ on which T_{c0} depends and the value of T_{c0} itself are determined by the relationship

$$\lambda = \frac{N(0)\,\langle I^2\rangle}{M\,\langle\omega^2\rangle}, \quad T_{c0} = \frac{\theta_D}{1.45}\exp\left(-\frac{1+\lambda}{\lambda-\mu^*}\right). \tag{7}$$

Here μ^* is a parameter that determines the depression of T_{c0} by the Coulomb repulsion of the electrons. In the series of $(TMTSF)_2X$ compounds with different X, the value of M is unchanged, the quantities a and hence $N(0)$ and I_Q in Eq. (6) vary weakly and nonmonotonically with increasing size of the anion. Therefore the increase in λ and T_{c0} with increasing size of the anion must involve the decrease in the quantity $\langle\omega^2\rangle \sim \theta_D^2$.

Apparently there are grounds for thinking that we face a tradeoff in synthesizing organic superconductors: a soft lattice with large values of λ, but with a tendency to dielectric instability with decreasing temperature, or a stiff lattice with not too large a value of λ. This tradeoff is also known for ordinary metallic superconductors (see Chap. 4 of Ref. 5). The potentialities for synthesis of new conducting organic crystals allow us to hope to come closer to an optimal structure (from the standpoint of T_c).

In closing we note that, on the whole, organic superconductors are well described by the BCS model, and there are now no clear proofs of the existence of them of any unique superconducting properties. However, we have practically no information on what phonons are essential for determining the parameter λ, and also on how the Coulomb interaction affects T_c. Tunneling measurements would enable us to get answers to these questions and to understand the potentialities of increasing T_c in organic superconductors.

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