Superconductivity and electronic properties of layered compounds

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The electrical, optical, and magnetic properties of layered compounds of dichalcogenides of transition metals and intercalated crystals are considered. Particular attention is paid to the anisotropy of these properties and to the analysis of the changes produced by intercalation. Experimental data are presented on the structural transitions in layered crystals and are examined from the point of view of the ideas concerning the charge-density wave. The bulk of the review is devoted to the superconducting properties of layered compounds (the critical temperature, the specific-heat discontinuity in the transition, the gap, the fluctuations above T_c, and the magnetic properties of ordinary and intercalated layered superconductors). The theoretical concepts that make it possible to describe the distinguishing features of the superconducting properties of layered and intercalated compounds are discussed (the effective-mass model and the model of Josephson interaction between layers).

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CONTENTS

1. INTRODUCTION

This review is devoted to a definite class of compounds, layered crystals of dichalcogenides of transition metals. These compounds are presently attracting wide attention because of a large number of exceptional properties. Foremost among them are strong anisotropy of the mechanical and electronic characteristics, due to the specifics of the crystal structure of layered compounds.[1-4] Owing to anisotropy, crystals of this class uncover a possibility of investigating most interesting effects of solid-state physics in their two-dimensional or almost two-dimensional manifestation. It is remarkable that the anisotropy of layered compounds can be most enhanced by intercalation.[1] Inasmuch as layered compounds intercalated by molecules include superconductors, we are presently able to investigate superconductivity in systems with almost two-dimensional motion of the conduction electrons.

The intercalation ability of dichalcogenides of transition metals, i.e., the ability to include atoms and molecules in the spaces between layers, is the basis for hopes of realizing high-temperature superconductivity via the exciton mechanism proposed by Little[5] and Ginzburg.[6] In essence, the intercalation ability of layered compounds was in itself observed by Gamble et al.[7] in connection with searches for the possible realization of the exciton mechanism of superconductivity. The class of intercalated compounds is practically unlimited, since there are many molecules and atoms that can be introduced into layered dichalcogenides crystals. In particular, crystals with alternating metallic and semiconducting layers are apparently the most promising from the point of view of realization of the exciton mechanism of superconductivity. It is likewise not excluded that combination, on a microscopic scale, of metallic layers with superconducting layers or with layers of complex molecules can lead to crystals with entirely new electronic properties.

Layered compounds have by now already found practical applications in devices such as superconducting quantum interferometers, where they are used as weak-coupling links, since they can be produced in the form of very thin films.[8] The possibility of realizing Josephson interaction between layers of a layered compound through intercalation uncovers very attractive prospects for an even wider practical application of crystals of this class.

Finally, structure transitions with formation of charge-density waves have been observed most recently in layered compounds.[9] Transitions of this type were hitherto observed only in quasi-one-dimensional crystals (the Peierls transition in planar-quadratic mixed-valence platinum complexes[10]). In the one-dimensional case, however, these are inevitably metal—insulator transitions. In layered systems, the low-temperature phase can become semimetallic or remain metallic, and if the

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[1] Intercalation is the implantation of atoms or molecules in crystals.

properties of the transitions turn out to be different than in quasi-one-dimensional crystals.

The present review is devoted to the electronic properties of layered metals and semimetals and, to a considerable degree, to the superconducting properties of layered compounds. We are interested primarily in how the electronic properties of layered crystals are changed by intercalation, and in those particular superconducting properties of layered compounds which distinguish them from ordinary isotopic or weakly-anisotropic superconductors. In addition to the experimental data on superconductivity, we shall discuss also those theoretical concepts and models which were proposed for the description of the superconductivity of layered systems with almost two-dimensional motion of the electrons. We shall not consider in detail the crystal structure of layered compounds—these data are contained in the reviews of Hulliger, Wilson, and Yoffe[1-3]. Detailed information on layered semiconductors is contained in the reviews[2,3] and the specifics of the mechanical properties are dealt with in the review by Kalikhman and Umanskiĭ.[4]

2. STRUCTURE OF LAYERED DICHALCOGENIDES OF TRANSITION METALS AND INTERCALATED COMPOUNDS

A. Dichalcogenides of Transition Metals

The general formula for layered dichalcogenide compounds is MX_2, where M is a transition metal from groups IV—VII and X = Se, S, or Te. The crystals of these compounds consist of layers, each of which is a sandwich of two sheets of halogen atoms X with a sheet of metallic atoms M between them. The bond between the metal atoms and the halogens in the sandwich is strong (predominantly covalent), and the atoms M and X form a two-dimensional hexagonal lattice in the sandwich. The MX_2 layers are coupled with one another in the crystal by weak Van der Waals forces. The crystal structure is shown schematically in Fig. 1.

Depending on the relative arrangement of the two sheets of the X atoms, two different crystal structures are produced within the X-M-X sandwich. In one of them, six X atoms surround the M atom, forming an octahedron, and in the other they form a trigonal prism (Fig. 2). The weak Van der Waals interaction of the layers admits of various methods of stacking the MX_2 sandwiches in the crystal along the axis perpendicular to the layers (the c axis). Therefore many layered compounds exist in several modifications. The most widespread stack types are shown in Fig. 3. The stack is characterized by a

number, a capital letter, and additional symbols if the first two symbols do not define the structure completely (1T, 2H, 2R, 4Ha, 4Hb, and 6R). The number is that of the layers in the unit cell, the capital letter characterizes the type of crystal symmetry (T—trigonal, H—hexagonal, R—rhombohedral). In phase 1T inside the sandwich the surrounding of the metallic atom is octahedral, in 2H, 3R, and 4Ha it is trigonal. In the modifications 4Hb and 6R sandwiches with octahedral and trigonal stacking alternate.

Since the interaction of the MX_2 layers is weak, it is not surprising that the physical properties of layered compounds are determined predominantly by the lattice structure inside the sandwich. The three modifications of TaS_2 demonstrate the strong dependence of the electronic properties of layered compounds on the type of the crystal structure inside the layer. The crystals 1T—TaS_2 with octahedral stacking of the Ta and S atoms in the layer are semiconductors or, more accurately, semimetals in which the conductivity increases weakly with increasing temperature ($\sigma_{\parallel}^{-1} \partial \sigma_{\parallel}/\partial T = 4.0 \times 10^{-3}$ °K^{-1} at T = 300°K for the conductivity $\sigma_{\parallel}$ along the layers). The crystals 2H—TaS_2 with trigonal stacking are metals. Layers with trigonal and octahedral surroundings alternate in the compound 4Hb—TaS_2, and in these crystals the conductivity along the layers is metallic because of the trigonal layers semimetallic transverse to the layers[11] (Fig. 4). This difference between the electronic properties of crystals with trigonal and octahedral stacking is preserved also for other dichalcogenides of Ta and Nb.

The anisotropy of the electronic properties of all the layered compounds is connected primarily with the fact that the electrons can move freely inside the layers, but between the layers the overlap of the electronic wave functions is weak because of the Van der Waals character of the layer interaction. Of greatest interest are layered compounds in which the anisotropy is extremely strong and leads in essence to almost two-dimensional

FIG. 3. Structure of different modifications of hexagonal layered compounds (1120 planes).

FIG. 1

FIG. 2
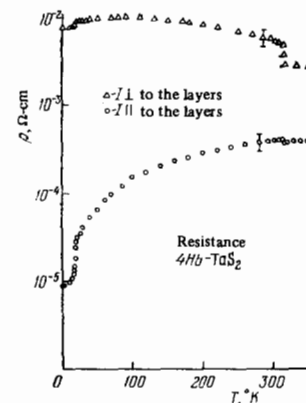
FIG. 4. Resistance of 4Hb-TaS_2 perpendicular and parallel to the layers. [11]
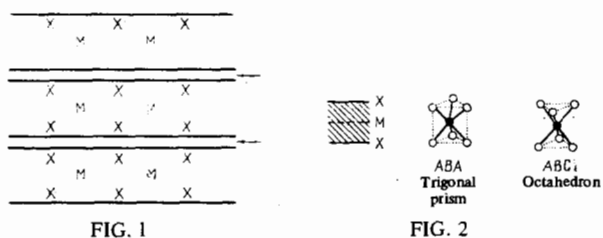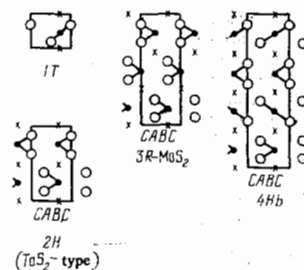
FIG. 1. Structure of layers in dichalcogenides of transition metals. The view is in a direction parallel to the layers. The arrows indicate the Van der Waals bonding.

FIG. 2. Mutual arrangement of the atoms M and X in the coordination cell inside the sandwich. ABA—trigonal prism, ABC—octahedron.

motion of the electrons in the crystal. Thus, in crystals of the semiconductor $3R-MoS_2$ optical observations seem to indicate the existence of two-dimensional excitons.[12] As already noted, a strong anisotropy of the kinetic properties is observed in $4Hb-TaS_2$. Finally, the existence of superconducting layered compounds (NbS_2 with critical temperature $T_c = 6.3°K$, $NbSe_2$, TaS_2, and $TaSe_2$) makes it possible to investigate superconductivity in systems that are close to two-dimensional (films consisting of several atomic layers)[2)] and in three-dimensional crystals with extremely anisotropic electron motion. The first possibility was realized by Frindt[13b], who observed a decrease of T_c from 7 to 4.5°K when the num-number of layers in $NbSe_2$ was decreased from 5 to 2. However, with the exception of T_c, the superconducting properties of these films have not yet been investigated. The crystals $4Hb-TaS_2$ permit an investigation of the superconductivity of the motion of the electrons in dif- ferent directions is different, but all that is known in this case so far is the value of T_c (2.9°K).[14] The anisotropy of the motion of the electrons in the most widely investigated layered superconductors $2H-NbSe_2$ and $2H-TaS_2$ is not very strong (the conductivity across the layers remains metallic). The anisotropy of these crystals, however, can be tremendously increased by intercalation with molecules.

B. Intercalated Layered Compounds

The weak Van der Waals bonds between the layers in dichalcogenides makes it possible to introduce extraneous atoms or molecules in the space between these layers. By now, a large number of intercalated compounds of dichalcogenides of Nb and Ta have been obtained with molecules,[7,15-17] ammonia[14,15], metals[18] metals and ammonia[14a], and hydrogen[19].

Layered compounds intercalated with molecules have the formula MX_2 (molecule)$_r$, where r is a fraction, mostly in a form close to $1/n$ (n is an integer). When the molecules are introduced the distance between the MX_2 layers increases and reaches 56 Å in the TaS_2 (octadeclyamine)$_{1/3}$[15] (the distance between layers in $2H-TaS_2$ is approximately 3 Å). The structure of this compound is shown schematically in Fig. 5. Sufficiently detailed x-ray data on the arrangement of the molecule layers are available so far only for $2H-TaS_2$ crystals with pyridine (C_6H_5N).[20b] In this intercalated compound, the planar pyridine (Py) molecules are arranged perpendicular to the layers, and the mutual disposition of the neighboring MX_2 layers differ somewhat from that in $2H-TaS_2$. The pyridine molecules between the TaS_2 layers form a rectangular superlattice with unit cell $2a\sqrt{3} \times 13a$, where a is the dimension of the hexagonal unit cell inside the TaS_2 layer. The complete unit cell of the intercalated crystal corresponds to the formula $TaS_2(Py)_{6/13}$ rather than $TaS_2(Py)_{1/2}$ (for brevity we shall henceforth write $1/2$ in the formula of the compound rather than $6/13$).

All the intercalated organic molecules are of the type of Lewis bases. They contain nitrogen with two unbound electrons and therefore have donor properties. A hypothesis was advanced in[16] that the electrons from the nitrogen molecule go over partially to the conduction band of the dichalcogenide layers and that this is the cause of the lowering of the system energy by intercala-
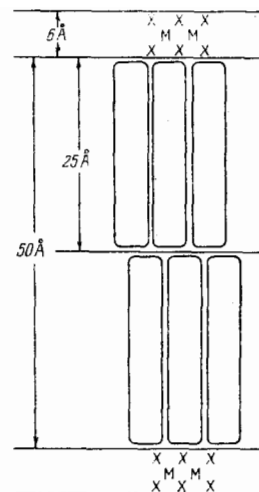

FIG. 5. Arrangement of the molecules of the octadecylamine in the compound TaS_2 (octadecylamine)$_{1/3}$.[20a]

tion. In accordance with this hypothesis, the molecule "sticks" to the layer as a result of the bond between the N atom of the molecule and the group of atoms M and X of the layer. Numerous experimental data confirm the hypothesis of charge transfer from the molecule to the MX_2 layer, and this hypothesis is the basis for the calculation of the change of the electronic characteristics of the molecule and of the conducting layer.[21] In fact, a certain correlation is observed between the ability of the molecule to intercalate in dichalcogenides and its ionization potential,[16] although the energetics of the intercalation depends also on a number of other factors.[17,21] A decrease of the electron density at the N atom of the molecule was revealed by data on the photoelectron emission induced by x-rays in $TaS_2(Py)_{1/2}$[16]. The change in the NMR spectrum of $NbS(Py)_{1/2}$ crystals can also be interpreted by assuming that the charge is transferred from the Py molecule to the conduction band of NbS_2 layers (according to these data, approximately 0.2 electron per Nb atom is transferred)[22]. The transfer of part of the electrons from the molecule to the dichalcogenide layers leads to a change in the electron density of the conducting layers and to the appearance near these layers of charged nitrogen groups at distances somewhat closer than the Van der Waals distances. These two factors, and also the electric field of the dipoles of the intercalated molecules, change the electron-phonon characteristics of the conducting layers and, as we shall show below, these changes are clearly seen when the magnetic susceptibilities and the critical temperatures T_c of the initial and intercalated layered compounds are compared.

Introduction of molecules between the conducting layers leads to an appreciable decrease of the overlap of the electron wave functions of different layers, if the molecule sticks to one MX_2 layer (for example in the compound $TaS_2(Py)_{1/2}$). According to the data of[23,24], introduction of Py into $2H-TaS_2$ increases the conductivity anisotropy from 10 to a value exceeding 10^5. In systems with such an isotropy, the motion of the electrons becomes practically two-dimensional. At the same time, the superconductivity does not vanish when the 2H-modifications of TaS_2, NbS_2 and $NbSe_2$ are intercalated with molecules and $4Hb-TaS_2$ is intercalated with ammonia, and in these systems the superconductivity can become quasi-two-dimensional.

The superconducting properties of layered metals are preserved also when they are intercalated with metal

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[2)]In principle one could obtain two-dimensional superconductivity over Tamm surface levels.[13a]

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atoms[18] and with both metals and ammonia[14]. In most cases the intercalation with metal atoms lowers T_c. However, introduction of iron atoms in 2H—TaS₂ leads to an increase of T_c to 3°K in Fe$_{0.05}$TaS₂ and to an appreciable increase of the anisotropy of the upper critical field.[14b]

The crystals of the 2H and 3R modifications of MoS₂, ZrS₂, HfS₂, WS₂ and WSe₂ intercalated with alkali-metal atoms[25-27] and with atoms of alkali-earth metals and Yb with ammonia[28] are also metals and superconductors. The initial layered compounds in this case are semiconductors with spectra of the exciton type.[2,3,12] Intercalation of MoS₂ with K, Rb, Cs, or Sr atoms results in the stoichiometric compounds K$_{0.4}$MoS₂, Rb$_{0.3}$MoS₂, Cs$_{0.3}$MoS₂, and Sr$_{0.2}$MoS₂, with critical temperatures of about 6°K. Compounds with Li and Na have no definite stoichiometry, and have $T_c \approx 4°$K. In the compounds A$_x$(NH₃)$_y$MoS₂ with A = Ca, Ba, Yb, or Sr the critical temperature does not exceed 5.7°K. According to x-ray structure data[52] intercalation increases the distance between the MoS₂ layers by 2—3.5 Å, and the parameter a of the two-dimensional lattice in the layer is increased by approximately 1%. An x-ray structure analysis[29] shows that the Na atoms and ammonia molecules are present between all the MoS₂ layers in the crystals Na$_x$(NH₃)$_y$MoS₂, and occupy the empty places inside the octahedron made up of the S atoms of neighboring layers. The intercalated atoms together with the impurities form a superstructure of orthorhombic symmetry, and intercalation with ammonia contributes to ordering of the impurities. More detailed information on the arrangement of the intercalated atoms is still lacking. Nor are the electronic characteristics of these compounds known, with the exception of the dependence of H_{c2} on the temperature in the crystals Cs$_{0.3}$MoS₂ and Sr$_{0.2}$MoS₂. According to these data, the anisotropy of the electron motion in these compounds is high, and quasi-two-dimensional superconductivity can also be realized in them (see Chap. 7).

3. ELECTRONIC PROPERTIES OF LAYERED METALS

We consider now the electronic properties of layered metals and intercalated compounds in the normal state. We are interested primarily in the anisotropy of the crystals and in those changes of the electronic properties which are observed after intercalation. In Table I are gathered the experimental data on T_c, on the conductivities $\sigma_{||}$ and $\sigma_\perp$ along and across the layers, on the Seebeck coefficient S, on the coefficient γ in the electronic term of the specific heat, and on the electron concentration N determined from the Hall effect (at low temperatures the sign of the Hall coefficient R_H corresponds to electron motion).

A. Kinetic Properties

We note that the temperature dependence of $\sigma_\perp$ of the crystals TaS₂(Py)$_{1/2}$ investigated in[23] duplicates exactly the variation of the conductivity $\sigma_{||}$, so that there is no doubt that the conductivity across the layers was determined by short circuits (due to the structure defects) between the conducting layers. It appears that the intrinsic anisotropy of the conductivity in the compound TaS₂(Py)$_{1/2}$ greatly exceeds that indicated in the table.

It is seen from the conductivity data that the anisotropy in 2H—TaS₂ and 2H—NbSe₂ is not very strong, and

TABLE I

Compound	T_c, °K	$\sigma_{||}$, Ω^{-1} cm^{-1}		$\sigma_{||}/\sigma_\perp$		S, μV/°K ($T = 300$ °K)	γ, mJ/mole·°K	N, cm^{-3} ($T = 4.2$ °K)	Reference
		$T < 10$ °K	$T = 300$ °K	$T < 10$ °K	$T = 300$ °K				
2H-TaS₂	0.8—2	10⁵	6.7·10³	28	13	—7	8.5±0.1	1.5·10²²	23, 30—32
2H-TaS₂ (Py)$_{1/2}$	3.2—3.7	(0.17—1)·10⁺⁵	3.3·10³	10⁵	7·10⁴	—7	8.9±0.4		18, 23, 24, 32
4Hb-TaS₂	2.9	10⁵	2.5·10³	10³	10				11, 33
2H-NbSe₂	7—7.4	(0.6—2)×10⁵	7·10³	20—50	30	—12	20.5	1.55·10²²	2, 3, 31, 34—36
2H-TaSe₂	0.15	10⁵	7.5·10³			—13	5.5		2, 31, 37

the temperature dependence of $\sigma_\perp$ shows that the conductivity across the layers in these compounds has a metallic character (the $\sigma_\perp(T)$ relation in non-intercalated crystals does not duplicate the $\sigma_{||}(T)$ relation, and the anisotropy $\sigma_{||}/\sigma_\perp$ indicated in Table I is intrinsic). After intercalation, the conductivity along the layers and the Seebeck coefficient remain practically unchanged (at room temperature, $\sigma_{||}$ is decreased by a factor of two as a result of intercalation, because the concentration of the carriers is decreased to one-half when the distance between layers increases from ≈ 3 Å in TaS₂ to ≈ 6 Å in TaS₂(Py)$_{1/2}$). At the same time, $\sigma_\perp$ decreases by more than five orders of magnitude, to a value 0.05—0.15 Ω^{-1} cm^{-1} at 20°K.[23,24] At so low a conductivity, the electrons undoubtedly move between the layers by hopping, as is apparently evidenced by the decrease of $\sigma_\perp$ observed by Thompson at T < 20°K.[24]

Under the influence of pressure, the anisotropy of the conductivity of the crystals 2H—NbSe₂ and 2H—TaS₂ decreases, since the dichalcogenide layers come closer together. From the data of[38] at T = 300°K, the anisotropy of the conductivity of NbSe₂ decreases from 30 to 18 as the pressure p increases from 0 to 30 kbar. At higher pressures, a structure transition takes place, after which the anisotropy continues to decrease with increasing pressure (linearly) and should vanish at 50 kbar.

B. Optical Properties

Measurements of the reflectivity or absorption in layered-compound crystals reveal clearly a plasma edge due to the reflection by the conduction electrons. Detailed measurements of the optical-absorption coefficient of 2H-NbSe₂ crystals, as a function of the frequency at 2°K, made it possible to determine the frequency dependence of the dielectric-constant component $\epsilon_{||}$ parallel to the layers, and from it the plasma frequency[39]. The expression used for $\epsilon_{||}(\omega)$ is

$$\varepsilon_{||}(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega[\omega + (i/\tau)]}, \qquad \omega_p^2 = \frac{4\pi N e^2}{m_{||}}, \qquad (1)$$

where ϵ_∞ is the dielectric constant of the internal electrons, ω_p is the plasma frequency, N is the electron concentration, τ is the relaxation time, and $m_{||}$ is the effective mass of the electron for motion along the layers. The best agreement with the experimental data were obtained with the parameters $\hbar\omega_p$ = 1.5 ± 0.2 eV, $\hbar\tau^{-1}$ = 0.12 ± 0.02 eV, and $\tau_\infty = 2.7 \pm 0.4$. Using the value N = 1.55 × 10²² cm⁻³, Bachmann, Kirsch, and Geballe obtained $m_{||}$ = 9.7 m_e (m_e is the mass of the free electron).

A shift of the plasma absorption edge following inter-

calation of $NbSe_2$ and TaS_2 with molecules was observed by Beal and Liang.[17] In most cases, a shift towards lower frequencies was observed. Similar measurements were made in[40] on the crystals $TaS_{1.6}Se_{0.4}$, $TaS_{1.6}Se_{0.4}(Py)_{1/2}$, and $TaS_{1.6}Se_{0.4}(aniline)_{3/4}$. The plasma frequency of the intercalated compounds $TaS_{1.6}Se_{0.4}$, calculated with the aid of the Drude formula (1), was lower than in the initial compound, owing to the increase of the distance between the conducting planes and the corresponding decrease of the carrier density. Assuming that the molecules act like a dielectric liner that moves the metallic layers apart (but does not change them) Benda Revelli, and Phillips obtained good agreement between the experimental data and the calculated values of ω_p in the case of a compound with pyridine (the agreement was only approximate for aniline).

The optical anisotropy of metallic layered compounds was investigated only for $2H-NbSe_2$ crystals by Liang.[41a] The reflectivity of the crystals was measured with the electric-field vector parallel and perpendicular to the layers. The value of ω_p was estimated approximately from the position of the plasma edge (without allowance for damping) and the estimates yielded $m_\parallel \approx 3.8m_e$ and $m_\perp/m_\parallel \approx 1.4$ at $78°K$. It appears that these estimates are not accurate enough, since the results for $m_\parallel$ differ strongly from that obtained in[39].

The intercalation of TaS_2 and of semiconducting layered compounds (MoS_2, HfS_2) with molecules leads to a change in the frequencies of the interband transitions in these crystals. An experimental investigation of these changes in the absorption spectrum makes it possible to determine the parameters that characterize the bonds between the intercalated molecules and the dichalcogenide layers within the framework of the charge-transfer concepts.[21]

It would undoubtedly be of interest to be able to measure $\epsilon_\perp(\omega)$ in intercalated compounds. Thus, in quasi-one-dimensional crystals $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$, the plasma edge, depending on $\epsilon_\perp(\omega)$, is not observed up to frequencies $\hbar\omega \approx 6$ eV.[10] i.e., the motion of the electrons across the chains is not metallic at frequencies $\hbar\omega < 6$ eV. A similar picture could be observed also in layered compounds intercalated with molecules.[3]

C. Magnetic Susceptibility and Specific Heat

The coefficient γ of the electronic-specific-heat term that is linear in the temperature yields direct information on the density of states $N(0)$ on the Fermi surface, in accordance with the relation

$$\gamma = \frac{2}{3}\pi^2 k_B^2 N(0),\qquad(2)$$

which is valid in the Landau model of a Fermi liquid. Taking into account the electron-phonon interaction, the right-hand side of the expression for γ contains the factor $(1 + \lambda)$, where λ is the dimensionless electron-phonon interaction constant. Since λ is small $(0.2-0.4)$, relation (2) makes it possible to estimate $N(0)$ from the

experimental value of γ with sufficient accuracy. It is seen from Table I that within the limits of the experimental errors the values of γ (and of $N(0)$) remain unchanged when TaS_2 is intercalated with pyridine.

The magnetic susceptibility of transition-metal compounds yields less unambiguous information on the electronic system, since the measured quantity is a sum of the contributions χ_{dia} of the diamagnetism of the ion core, χ_P of the Pauli paramagnetism, and χ_V of the Van Vleck paramagnetism[43]:

$$\left. \begin{aligned} \chi &= \chi_{dia} + \chi_P + \chi_V, \\ \chi_P &= \tfrac{1}{2}g^2\mu_B^2 N(0)\,[1 - U_{eff}n(0)]^{-1}, \\ \chi_{ij,V} &= \mu_B^2 \sum_{m,m'} \int \frac{d\mathbf{k}}{(2\pi)^3}\,\frac{f(E_m(\mathbf{k})) - f(E_{m'}(\mathbf{k}))}{E_{m'}(\mathbf{k}) - E_m(\mathbf{k})} \\ &\quad \times \langle m, \mathbf{k}\,|\,L_i\,|\,m', \mathbf{k}\rangle \langle m', \mathbf{k}\,|\,L_j\,|\,m, \mathbf{k}\rangle, \end{aligned} \right\} \qquad(3)$$

where U_{eff} is the effective atomic exchange interaction, $n(0)$ is the density of states per atom (the Stoner factor in χ_P reaches values $2-4$), L is the orbital-angular-momentum operator, m and m' are the indices of the electronic bands corresponding to the d levels of the transition metal, and f is the Fermi distribution function. The value of χ_{dia} for transition ions is quite difficult to estimate, but the diamagnetic contribution of dichalcogenide layers is approximately the same for different modifications and for the same composition, and is not altered by intercalation. Therefore the change of the magnetic susceptibility of the layers following intercalation or following a transition to another modification is due mainly to the change of χ_V, since the Van Vleck paramagnetism is highly sensitive to changes of the electronic structure.

The magnetic-measurement data are listed in Table II. In addition, to the measured values of $\chi_\perp$ and $\chi_\parallel$ (magnetic field perpendicular or parallel to the layers) and of $\bar{\chi}$, the table lists for comparison also the results of calculations of χ_P with $N(0)$ from data for γ without allowance for the Stoner factor. The quantity $\bar{\chi}$ is the susceptibility of powdered samples. Owing to the preferred orientation of the crystal, this quantity can differ somewhat from the true average susceptibility $(2\chi_\perp + \chi_\parallel)/3$, and this difference is indeed observed for $TaS_2(Py)_{1/2}$. It is seen from Table II that $\chi_\perp$ greatly exceeds $\chi_\parallel$ for Ta compounds. This difference is undoubtedly connected with the Van Vleck contribution. From calculations of the band structure (see Sec. b of Chapter IV below) it follows that the $2H-TaS_2$ conduction band is made up of the orbitals d_{z^2}, $d_{x^2-y^2}$, and d_{xy} of the Ta atom.[4] Located higher in energy are two bands of the same orbitals, and still higher the bands d_{xz} and d_{yz}. The contribution to $\chi_V(\perp)$ is determined by that matrix element of the operator L_z which connects the bands that are closest in energy (d_{xy} and $d_{x^2-y^2}$, and therefore $\chi_V(\perp) > \chi_V(\parallel)$. From a comparison of the values of $\bar{\chi}$ for different modifications of TaS_2, we see that $\bar{\chi}(4Hb) = [\bar{\chi}(1T) + \bar{\chi}(2H)]/2$, i.e., the interaction of the layers has little effect on the electronic properties of octahedral and trigonal layers. The fact that $2H-TaS_2$ and $4Hb-TaS_2$ have approximately equal values of $\sigma_\parallel$ (per conducting trigonal layer) and a similar temperature dependence of $\sigma_\parallel$[11,23] confirms this conclusion.

Table III lists the values of $\bar{\chi}$ at $50°K$, of the lattice

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[3]In intercalated compounds, as well as in quasi-one-dimensional crystals, one can observe in principle a reflection peak at the plasma frequency at incidence angles close to normal.[41b] To this end it is necessary that the layers be perpendicular to the crystal surface and to the plane of incidence, and that the electric-field vector lie in the plane of incidence. Such a peak was already observed experimentally in the quasi-one-dimensional crystals $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$.[42]

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[4]Here and below, the z axis is perpendicular to the layers.

TABLE II

Compound	Measured quantity	Measurement results 10^{-6} cm³/mole	χ_T, 10^{-6} cm³/mole	Reference
1T-TaS₂	$\bar{\chi}$; 50 °K	−47		11
2H-TaS₂	$\bar{\chi}$; 50 °K	151	117	11
	$\bar{\chi}$; 300 °K	134		
	$\chi_{\perp}$; 300 °K	223		
	$\chi_{\parallel}$; 300 °K	89		
2H-TaS₂ (Py)₁/₂	$\bar{\chi}$; 50 °K	69	123	20a
	$\chi_{\perp}$; 50 °K	167		
	$\bar{\chi}_{\parallel}$; 50 °K	33		
4Hb-TaS₂	$\bar{\chi}$; 50 °K	56		11
1T-TaSe₂	$\bar{\chi}$; 50 °K	−38		37
2H-TaSe₂	$\bar{\chi}$; 50 °K	110	76	37
2H-NbSe₂	$\bar{\chi}$; 50°, 300 °K	185—200	283	18, 44

TABLE III

| Compound	$\bar{\chi}$, 10^{-6} cm³/mole	χ_{dia} (of molecule) 10^{-6} cm³/mole	$\bar{\chi}$ (TaS₂), 10^{-6} cm³/mole	a, Å	d, Å
2H-TaS₂	151	0	151	3.315	6
TaS₂ (collidine)₁/₆	109	−79	122	3.319	9,6
TaS₂ (2-phenyl-pyridine)₁/₅	55	−84	72	3.328	12
TaS₂ (picoline)₁/₃	83	−56	102		12
TaS₂ (pyridine)₁/₂	69	−50	94	3.326	12
TaS₂ (aniline)₃/₄	47	−64	95		18

parameter a inside the layer, and of the distance d between layers of a number of intercalated compounds of TaS₂.[20a] The table gives also the values of $\bar{\chi}$ for TaS₂ in these crystals; these values show that the magnetic susceptibility of the crystals is strongly altered by the intercalation (at the same time γ, and consequently also N(0), remains practically unchanged when intercalated with pyridine). The data of Table III confirm the conclusion that χ is practically independent of the interaction of the layers. Therefore the change of χ by intercalation is due mainly to their interaction with the molecules. This interaction changes not only the electronic characteristics, but also the crystal structure of the layer (in particular, the parameter a). We note that according to the data of Table III there is a clear-cut correlation between the changes of $\bar{\chi}$ (TaS₂) and the parameter a. In Sec. c of Chap. V we shall show that the changes produced by intercalation in the system of conduction electrons of the layers can be revealed also by the change of T_c. Since the changes in the electron systems are in general small (the corresponding energies are low in comparison with ϵ_F), it is not surprising that only such sensitive quantities as T_c and χ_V are noticeably altered by intercalation.

4. STRUCTURAL TRANSITIONS AND BAND STRUCTURE OF LAYERED COMPOUNDS

A. Experimental Data on Transitions Between Polytypes

Reversible structural transitions take place within the framework of one and the same modification (1T, 2H, or 4Hb). The index 1T (just as 2H or 4Hb) pertains therefore to several polytypes, the structures of which differ slightly from one another, but are close to the simple structure C6 shown in Fig. 3. Analogously, the polytypes of the 2H modifications of Nb and Ta are close to the structure C27 shown in the same figure. In contrast to transitions between polytypes, transitions be-

FIG. 6. Behavior of the susceptibility $\bar{\chi}$, of the resistivity ρ, and of the Hall coefficient R_H in structural transitions in 2H modifications of chalcogenides of Nb and Ta (schematic).
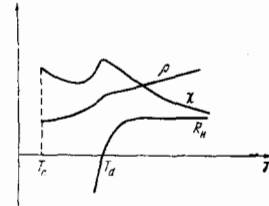
tween modifications are irreversible and are observed at higher temperatures. Thus, the 2H → 1T transition occurs for TaSe₂ at 1100°K, and the enthalpy jump for it is approximately one order of magnitude larger than for the transition between the polytypes 1T at T_d = 473°K.[37]

Structural transitions between metallic polytypes are observed in the 2H modifications of TaS₂, TaS, and NbSe₂ at T_d = 117.75 and 35°K, respectively. It appears that these transitions are of first order but very close to second. Thus, in 2H—TaS₂ the jump of the enthalpy is only ≈ 1 cal/mole. The transitions are manifest primarily in changes of the kinetic and magnetic properties of the metals. Schematically, the features of the variation of χ, of the resistivity ρ, and of R_H at the transition point T_d are shown in Fig. 6 on the basis of the data of [44, 45] for NbSe₂, of [44] for TaSe₂, and of [23] for TaS₂.[5] According to the data of [47], a jump of T_c (7.2 → 7.4°K) is observed in 2H—NbSe₂ at a pressure p = 1 kbar. Since the Hall coefficient is positive in a phase that is stable at p > 1 kbar, one can assume that the jump of T_c corresponds to the same structural transition as the transition at 35°K and p = 0. If this is the case, then T_d in 2H—NbSe₂ decreases with increasing pressure to ≈ 7°K at p = 1 kbar.

In the 1T and 4H modifications, the structure transitions are of first order. Table IV lists the changes of the enthalpy, of the resistivity ρ, of the volume V, and of the magnetic susceptibility at the transition point T_d. The character of the variation of ρ(T) in the transitions in 4Hb—TaS₂ is shown in Fig. 4. In 1T—TaS₂, just as in 4Hb—TaS₂, for a current perpendicular to the layers, the resistance decreases slowly with increasing T in the intervals 0—190°K and 190—348°K. According to the experimental data[37, 49] the specific heat of 1T—TaSe₂ and 1T—TeS₂ decrease at the lowest temperatures with decreasing T more slowly than T. This dependence of the electronic specific heat on the temperature offers evidence that the state density N(ϵ) near the Fermi level varies rapidly with energy ϵ, increasing as $\epsilon \to 0$ (see, e.g., [50]). This N(ϵ) dependence should manifest itself in the magnetic properties as a growth of the paramagnetic susceptibility as T → 0 at a slower rate than called for by the Curie law. Therefore magnetic measurements in 1T—TaSe₂ and 1T—TaS₂ crystals at infralow temperatures (similar to the measurements of [50]) would be capable of confirming the existence of a sharp maximum in the state density at the Fermi energy.

We now consider the experimental data concerning the type of lattice change that occurs in structural transitions in 2H and 1T modifications. In 2H—NbSe₂, according to the NMR data, at 4°K[45] there exist in the lattice two types of Nb atoms which are not equivalent in charge, and according to the structural data[51a] the lattice period quadruples in the transition. For transi-

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[5] According to [46] an approximate jump of 1.5% is observed in the resistivity of 2H-TaS₂ at the transition point.

TABLE IV

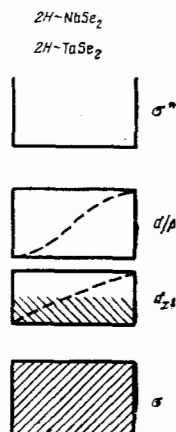| Compound	T_d, °K	dT_d/dp °K/kbar	ΔH, cal/mole	$\rho_\pm = \dfrac{\rho_+/\rho_-}{\rho}(T_d \pm 0)$	$\Delta V/V$, %	$\Delta\chi \cdot 10^{-6}$, cm³/mole	Reference
1T-TaS₂	190		57	0.1		+1.85	11, 48
	348	−2.8	31	0.5	0.056	+1.6	
1T-TaSe₂	437	−4.7	320	0.25	0.35	−1.8	37
4Hb-TaS₂	20			1			11
	315	−5.5	110	1 along the layers, 0.2 perpendicular to the layers.	0.22	+0.9	

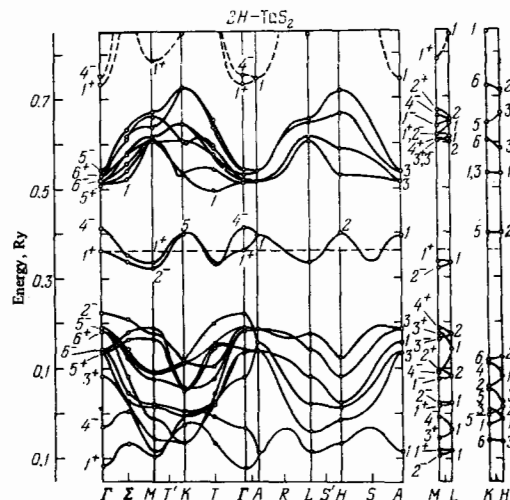FIG. 7. Arrangement of the energy bands in layered compounds of Ta and Nb. [2]

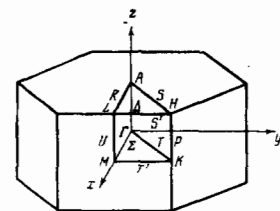FIG. 8. Electron energies in 2H-TaS₂, calculated by the method of augmented plane waves. [54]

FIG. 9. Brillouin zone for hexagonal Bravais lattice.

tions in 1T modifications, there are at present more detailed data, and they cast light on the causes of the structural transitions in layered compounds. Wilson et al.[9], in an investigation of the diffraction of electrons in 1T—TaSe₂, observed a superstructure inside the layers (against the background of the main C6 structure) with a period $\sqrt{13}a$, where a is the period of the basic hexagonal structure in the plane of the layer. According to[9,37], the true lattice is pseudohexagonal inside the layers. The deviations of the atoms from their positions in the ideal structure are small and range from 0.05 to 0.1 Å. In 2H—TaSe₂ below 117°K, a superlattice also appears, but with a period[6] 3a. In the series of compounds 1T—Ta$_x$Ti$_{x-1}$Se₂, the superlattice period decreases with decreasing x. This relation gives grounds for assuming that the appearance of the superlattice is connected with the singularities of the geometry of the Fermi surface. According to the theoretical premises[52,53] the presence of congruent sections on the Fermi surface in the high-temperature phase must inevitably lead to the appearance of a superstructure with decreasing temperature, and this effect, according to the hypothesis of[9], is the cause of the transitions between polytypes of layered compounds. Before we proceed to a more detailed discussion of the concepts concerning transitions of this type, it will be useful to consider the data on the band structure and the shape of the Fermi surface of layered compounds in their high-temperature phases (see Note 1 added in proof at the end of the article).

B. Structure of the Energy Beams of Layer Compounds

A schematic model of the band structure of layered compounds, on the basis of optical data, was proposed by Wilson and Yoffe[2], and is shown in Fig. 7 for 2H compounds of Nb and Ta. According to this model, the layer valence band σ and the upper band σ* correspond to binding and antibinding s-p orbitals of metals and halogens. The conduction band corresponds to d_{z^2} orbitals of the metal, and for the elements of the Vb group the conduction band is half-filled. Above the conduction band are located the bands d_{xy}, $d_{x^2-y^2}$ and the bands d_{xz}, d_{yz} in order of increasing energy. In the compounds of Mo and W with trigonal packing in the layer, the band scheme is the same, but the band d_{z^2} is completely filled, and these compounds are semiconductors (the energy gap in 2H—MoS₂ is 1.4 eV[54]). For dichalcogenides of group IV (Ti, Zr, Hf) there are no electrons in the d band, and these compounds are dielectrics with rather large gaps (2.0 eV in 1T—HfS₂[54]).

Subsequent numerical calculations have refined the energy scale and the symmetry of the wave functions of the different bands. The most complete calculations of the band structure of layered 1T—TaS₂ compounds with structure C6, of compounds 2H—TaSe₂ and 2H—NbSe₂ with structure C27, by the method of augmented plane waves (APW) were carried out by Mattheis[54], and this paper contains also a detailed comparison of the results of this method with the experimental data and with the results of other approximations. Figure 8 shows the energy levels of 2H—TaS₂, calculated at the symmetrical points of the Brillouin zone as indicated in Fig. 9. The straight dashed line shows the Fermi level, and the lower band corresponds to band σ on the scheme of Fig. 7, while the upper dashed band corresponds to the band σ*. As a result of hybridization, the d levels shift, and the two sub-bands turn out to be lower ones (the Fermi level passes through the lower one). These lower sub-bands consist of strongly hybridized functions d_{z^2}, d_{xy}, and $d_{x^2-y^2}$ of the Ta atoms (thus, at the point Γ the lower sub-band consists of the orbital d_{z^2}, and at the point K it consists of the orbitals d_{xy} and $d_{x^2-y^2}$).

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[6]According to [46,51b], a superlattice was observed also in 2H—TaS₂ crystals. Just as in TaSe₂, the period of the superlattice is approximately equal to 3a.

Hybridization leads to a strong narrowing of the lower sub-band, the width of which turns out to be of the order of 1 eV. Owing to the interaction of the layers, the energies at the points A, H, L and Γ, K, M are different, and, as seen from Fig. 8, this difference in the conduction bands reaches a maximum value at the points A and Γ.

To investigate the influence of intercalation on the band structure, Mattheis calculated also the energies of the hypothetical compound $2H-NbSe_2$ in which the layers are shifted along the c(z) axis by another 1.5 A. After such a "separation," the difference at the points A, H, L and Γ, K, M decreases by approximately a factor of five, and the band structure becomes practically two-dimensional. It follows also from the Mattheis results that all the singularities of the energy spectrum of the electrons in the conduction band can be accounted for with sufficient accuracy in the two-dimensional approximation. This conclusion is confirmed by the observation, in the reflection spectrum of the TaS_2 crystals, of van Hove singularities in the band structure, which are typical of electrons with two-dimensional motions (singularities of the saddle-point type [55]).

From a comparison of the Mattheis calculations with the data on photoemission [56-57] it follows that the APW method accounts sufficiently well for the structure of the d band, but it yields less accurate results for the relative placement of the bands σ, σ*, and d. Thus, according to the experimental data the lower d-sub-band intersects the band for $2H-TaS_2$ and $2H-NbSe_2$, although this intersection is small. The Mattheis calculations do not yield such an intersection. At the same time, the small width of the conduction band obtained by Mattheis agrees with the photoemission data (they yield a width less than 0.70 eV), and with the large electron effective mass as determined from measurements of the plasma frequency (see above).

We emphasize that all the structures calculated by Mattheis for $NbSe_2$ and TaS_2 are realized only in high-temperature polytypes. Therefore these calculations cannot yield a description of those low-temperature properties of layered metals and semi-metals which are sensitive to a high degree to the structure of the Fermi surface. However, the results of Mattheis yield information on the singularities of the Fermi surface of high-temperature polytypes, which by assumption [9] determine the appearance of a superstructure with decreasing temperature. The Fermi surface for $1T-TaS_2$ in the plane $k_z = 0$, obtained from the calculations of [54], is shown in Fig. 10 and indeed contains flat sections which can be joined through a shift by the vector q_0.

C. Charge-density Wave in Layered Compounds

If the Fermi surface has sections that can be made completely congruent by parallel displacement through a certain vector q_0, then the electron spectrum satisfies the condition

$$\varepsilon(k) - \varepsilon_F = -\varepsilon(k - q_0) + \varepsilon_F \qquad (4)$$

for the region of the electronic states k with energies close to the Fermi energy (as $\epsilon(k) \to \epsilon_F$). The condition (4) is a condition for the equality of the energies of the electron and hole with summary momentum q_0 and leads to a logarithmic singularity of the dielectric constant $\epsilon(\omega, q)$ at $\omega = 0$ and at $q = q_0$.[52] In particular, the condition (4) is satisifed if the Fermi surface has flat
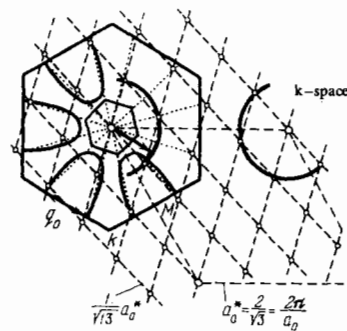

FIG. 10. Two-dimensional Fermi surface in $1T-TaS_2$. The figure shows also the vector q_0, which determines the radius of the diffuse scattering from the superlattices, and the Brillouin Zone corresponding to the superlattice. [9]

parallel sections. A similar singularity always takes place in a one-dimensional metallic system of the electrons, inasmuch as in such a system the Fermi surface consists of two points with wave numbers $\pm k_F$, and these can always be made congruent through a shift by the wave number $2k_F$ (the logarithmic singularity appears if the regions that can be made congruent by translation through a vector q_0 have the same dimensionality as the Fermi surface itself). In the case of an isotropic Fermi surface, translation by a vector q_0 with $|q_0| = 2k_F$ makes it possible to make congruent only two diametrically-opposite points of the Fermi surface, and a logarithmic singularity appears only in the derivative $\partial\epsilon(0, q)/\partial q$ as $q \to 2k_F$ (the Kohn anomaly of the dielectric constant). In a three-dimensional metal with spectrum (4), just as in a one-dimensional system of electrons, the logarithmic singularity of $\epsilon(0, q)$ at $q = q_0$ leads to the appearance of a sinusoidal shift of the atoms from the equilibrium positions of the initial lattice with decreasing temperature below T_d. The displacements are characterized by the wave vector q_0, and on the flat sections of the Fermi surface below T_d there appears an energy gap corresponding to Bragg reflections from the superstructure. This gap, however, can cover up only flat parallel sections of the Fermi surface. Therefore in the general case of a two-dimensional or three-dimensional lattice, when the Fermi surface consists not of flat sections only, the transition in which a superstructure (charge-density wave) appears is a metal—metal or metal—semimetal transition, depending on the areas of the covered sections of the Fermi surface. In the one-dimensional case, on the other hand, the analogous Peierls transition is always a metal—insulator transition ([10]).

In the 1T modification, the energy gap appears over a larger part of the Fermi surface. Thus, according to Wilson's calculation [37] for $1T-TaSe_2$ (they are based on the Mattheis results [54]), 12/13 of the Fermi surface is covered up on going from the hexagonal lattice with a period a to a pseudohexagonal one with period $\sqrt{13}a$. Therefore as a result of the appearance of the superstructure, the $1T-TaSe_2$ crystals are diamagnetic semi-metals at low temperatures. It appears here that on part of the remaining Fermi surface a singularity arises in the density of states and leads to the already mentioned anomalies of the electronic specific heat.

In the 2H modifications of $NbSe_2$, TaS_2, and $TaSe_2$ only a small part of the Fermi surface is covered up at the point T_d and the low-temperature polytypes remain paramagnetic metals (see Note 2 added in proof at the end of the article).

In the metal series NbSe₂, TaS₂, and TaSe₂, the covered part Fermi surface increases, inasmuch as T_d increases in this series and $d\rho/dT$ is smaller than T_d. The structure transition undoubtedly influences also on the superconducting properties of the 2H metals. According to the data of[47] in NbSe₂, following a pressure-induced transition from a low-temperature polytype to a high-temperature one, T_c increases by 0.2°K, and this difference is preserved also at normal pressure if the high-temperature polytype can be preserved (in a metastable state) when the pressure is removed. It appears that the T_c suppression due to the structural transition is even stronger in TaS₂ and TaSe₂, and this is the cause of the low values of T_c of these crystals.

According to the data of[20a, 23], intercalation of 2H—TaS₂ with collidine and picoline molecules lowers the height of the peak in the $\chi(T)$ plot at the point T_d in comparison with non-intercalated 2H—TaS₂ crystals, while in the case of TaS₂ (Py)₁,₂ crystals the peak of $\chi(T)$ and the kink in the (T) plot are practically nonexistent. After intercalation and following de-intercalation of the TaS₂ crystals, according to the communication[58], the singularity in the temperature dependence of the conductivity also vanishes. In the same study we observed an increase in T_c in the crystals TaS₂, TaSe₂, NbS₂, and NbSe₂ after bombardment with argon ions. After bombardment, the critical temperatures in TaS₂ and TaSe₂ reached 4.2 and 2.5°K, respectively, and the authors of[58] attribute this increase of T_c to the suppression of the structural transitions by the appearance of lattice defects. So far, however, there are no data on the temperature dependence of the Hall coefficient in intercalated and defect-containing crystals, so that it is impossible to state with full assurance that intercalation or bombardment with argon ions suppresses the structural transition. Nonetheless, this conclusion seems quite likely, for after intercalation the molecules change the period of the initial lattice in the layer (in which case violation of the condition (4) is possible), and furthermore intercalation causes deterioration of the crystal structure. In either case, the temperature T_d should decrease, and in the case of strong disturbances to the initial structure the transition may turn out to be completely suppressed[10, 59] (see Note 3 added in proof at the end of the article).

5. CRITICAL TEMPERATURE. SPECIFIC-HEAT JUMP AND GAP IN LAYERED SUERCONDUCTORS

A. Influence of Pressure on T_c

In the initial investigations of the superconductivity of layered compounds it was assumed that the critical temperature is determined by a strong degree by the interaction of the layers, and that when this interaction is increased the value of T_c should increase because of the suppression of two-dimensional fluctuations.[60] These arguments were based on the fact that in the compound Nb₁₊ₓNSe₂ the distance between layers increases with increasing x, and T_c decreases.[61] However, after T_c was measured as a function of the pressure in 2H—NbSe₂ and 3R—NbS₂, it became clear that the change of T_c is more readily correlated with changes of the parameter a inside the layer than the changes of the distance between the conducting layers.[62] Later on, Dzyaloshinskiĭ and Kats[63] have shown that in layered superconductors the fluctuations do not suppress the superconducting long-range order even at a very small

interaction between layers (see also Sec. a of Chap. 7). Sambongi[47b] applied unilateral compression of 2H—NbSe₂ along the c axis; it turned out that T_c decreases with increase of this compression. There is at present no doubt that the growth of T_c under pressure in 2H—NbSe₂ (28°K as the pressure is increased to 140 kbar[64-66]) is connected with the decrease of the lattice parameter a inside the layer.

B. Intercalation and the Problem of High-temperature Superconductivity.

Hopes of increasing T_c by intercalation are connected with the ideas of Little and Ginzburg concerning the exciton mechanism of superconductivity. According to the assumption in[6], it is necessary to produce a system in which the superconducting layers are joined with molecular or semiconducting layers. The polarization of the molecules or of the superconductor by the conduction electrons should lead to an effective attraction of the conduction electrons. Since T_c is proportional to the frequency of the excitations of the polarized system, one should expect an increase of T_c when the phonon mechanism (frequencies on the order of the Debye frequency) is replaced by the exciton mechanism (frequencies on the order of 0.1—0.3 eV). Two-dimensional systems[6] have here that advantage over one-dimensional systems[5] in that the fluctuations that destroy the superconducting long-range order are smaller in them[67]. However, $T_c < 6$°K in all the hitherto obtained intercalated compounds with molecules, and there are no indications that the superconductivity of these compounds is determined a non-phonon mechanism. Estimates of the effectiveness of the exciton mechanism in layered compounds with molecules[68] have shown that in such compounds the exciton mechanism is little effective in comparison with the phonon mechanism, owing to the localized character of the molecular excitations and hence of the impossibility of realizing a large momentum transfer on the order of $2k_F$, at a relatively low excitation energy on the order of 0.1 eV. This conclusion was in essence confirmed by Little,[69] who calculated the effectiveness of electron attraction by a conducting plane in the presence of a number of particular molecules near this plane. The interaction via the excitons turned out to be comparable in magnitude with the phonon interaction only when the molecules come within a distance R = 1.5 Å of the plane, and this is smaller than the Van der Waals distance (≈ 3 Å), and only at small values of $2k_F$ for the conduction electrons inside the layer ($2k_F = 0.33$ Å⁻¹, corresponding to $\epsilon_F \approx 0.1$ eV).[7]

More greatly promising from the point of the exciton mechanism of superconductivity can be crystals with alternating metallic and semiconducting layers. A large momentum transfer on the order of $2k_F$ at a relatively low energy of excitation on the order of 0.1 eV can be realized in them if the valence and conduction bands are separated by a momentum **g** with g $\approx 2k_F$. It appears that systems of this type and related systems of the sandwich type are the most promising from the point of view of the problem of high-temperature superconductivity[70]. The development of mixed crystals (TaS₂ with

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[7]At a small value of ϵ_F it is impossible to satisfy the condition that ϵ_F greatly exceed the energy of those excitations which ensure the exciton mechanism of the superconductivity. At the same time, only when this condition is satisfied does the attraction of the electrons due to exciton exchange exceed the Coulomb repulsion of the conduction electrons.

WS₂, NbSe₂ with MoS₂, etc.) is reported in[3], but there is still no information concerning their properties.

C. Critical Temperature for Intercalated Compounds

The most thoroughly investigated intercalated compounds are $2H-TaS_2$, in which T_c is higher than for the initial compound (from 2 to $4.5°K$, as against $0.8-2°K$ for $2H-TaS_2$; the situation for $NbSe_2$ and NbS_2 is reversed—intercalation lowers T_c to approximately $4°K$).

The intercalated compounds $2H-TaS_2$ prove, first, that T_c is independent of the distance between layers. Thus, for $TaS_2(octadecylamine)_{1/3}$ with distance 56 Å between layers, the value of T_c is approximately the same as for other intercalated compounds ($\approx 3°K$). Therefore the change of T_c by intercalation is connected mainly with the change of the electronic characteristics of the conducting layer (owing to the transition of part of the electrons from the molecules and to the action of the potential of the charged molecular groups). Indeed, a tendency to a decrease of T_c with increasing number of molecules per Ta atom was observed already in[16]. This tendency was confirmed after $2H-TaS_2$ intercalated with n-alkyl-amines were produced[15]. Linear molecules of this series differ only in the number of carbon groups, which have little effect on the donor ability of the nitrogen group of the molecules. It turned out that T_c decreases with increasing length of the molecule (from $4.2°K$ for NH_3 to $1.8°K$ for octylamine), until the molecules are parallel to the layers and the number of molecules per Ta atom decreases (the distance between the layers remains here practically constant). With further increase of the length of the molecules, starting with n-nonylamine, the molecules are already arranged perpendicular to the layers, the distance between layers increases with increasing length of molecules, and T_c remains practically unchanged.

The change of T_c undoubtedly depends on the type of the molecule, but at the present time it is not clear which are precisely the molecule electronic characteristics that determine T_c of intercalated compounds. We mention only that a correlation has been observed between the frequencies of the quadrupole resonance at the atoms of N molecules prior to their intercalation, on the one hand, and the increase of T_c of intercalated crystal $2H-TaS_2$, on the other.[71] We note that part of the increase of T_c is due to the change of the degree of perfection of the crystals following intercalation, inasmuch as the data of[16] show that after de-intercalation of the TaS_2 crystals the values T_c (1 to $1.5°K$), remained higher than those prior to intercalation ($\approx 0.8°K$).

As already noted above, MoS_2, WS_2, and WSe_2 are semiconductors, and no superconductivity was observed in them. Their intercalation with alkali metals and alkali-earth metals with ammonia yields crystals with values of T_c from 3 to $6°K$. In[25-28] the appearance of metallic properties after intercalation is attributed to a transition of the electrons from the metal atoms to the MX_2 layers (one of the d sub-bands then becomes partly filled).

D. Specific-Heat Jump, Size of Gap, and Applicability of BCS Theory to Layered Superconductors

Measurements of the specific-heat jump and of the energy gap in layered superconductors are of interest primarily because one can expect the strong anisotropy to give rise to deviations from the BCS theory in these compounds. Thus, the gap in these compounds can turn out to be anisotropic, i.e., its value can depend on the position of the momentum on the Fermi surface.

According to the BCS theory, the specific-heat jump Δc during a superconducting transition should amount to $2.43\gamma T_c$. A ratio $\Delta_c/\gamma T_c$ close to 2.4 was observed in $2H-NbSe_2$,[31] $2H-TaS_2$,[32] and $H_{0.06}TaS_2$.[20b] At the same time, in $TaS_2(Py)_{1/2}$ and $TaS_2(2.6$-dimethyl pyridine$)_{1/5}$ the ratio $\Delta c/\gamma T_c$ turned out to be equal only to 0.8 and 0.65, respectively.[32] It appears that additional measurements of the specific heat on single crystals are needed (in[32] they investigated powders) before it becomes necessary to forgo the BCS theory for the description of superconductivity in intercalated compounds with molecules.

Measurements of the transmission of light in thin $2H-NbSe_2$ crystals (of thickness 200—600 Å) at temperatures above and below T_c yielded for the optical gap values $2\Delta = 0.00215$ eV at $1.6°K$ and $2\Delta/k_BT_c = 3.7$ in accordance with the BCS theory.[72] Within the limits of errors, the measured values of the gap for light polarized along and across the layer were the same. Tunnel experiments by Morris and Coleman[105] yielded for $NbSe_2$ a mean gap value of approximately 0.00124 eV at $1.1°K$. This value could correspond to the gap for momenta perpendicular to the layers, but the results of Howard for the average gap in the same tunnel systems turned out to be different, and the gap value obtained by him is in agreement with the BCS theory.[73]

6. QUASI-TWO-DIMENSIONAL SUPERCONDUCTIVITY AND THE MODEL OF JOSEPHSON INTERACTION OF LAYERS

A. Quasi-two-dimensional Superconductivity

Let us determine first in which cases does the strong anisotropy of the motion of the electrons lead to a qualitatively new (quasi-two-dimensional) behavior of electrons in layered compounds. Let us consider some effects characterized by an energy ϵ_0 per electron. Then, with respect to this effect, the system of electrons can be assumed to be two-dimensional if the electron energy $\epsilon_\perp$ connected with its motion between the layers is much less than ϵ_0. In the opposite limiting case $\epsilon_0 \ll \epsilon_\perp$ we are dealing with ordinary anisotropy. For superconductivity, the characteristic energy is the value of the gap $\Delta(T)$ at a given temperature T. In the hopping mechanism of conductivity across the layers $\epsilon_\perp = \hbar/\tau_\perp$, where $\tau_\perp$ is the time of the jump between two neighboring layers, and the condition of the quasi-two-dimensional superconductivity takes the form[74,75]

$$\frac{\hbar}{\tau_\perp} \ll \frac{\Delta^2(T)}{T_c} \approx T_c - T. \tag{5}$$

If the condition (5) is satisfied, then, when considering those superconducting properties which are not connected directly with the motion of the electrons between layers, the electron system can be regarded as two-dimensional. At the same time, the motion of the superconducting electrons between the layers will be of the Josephson type in this case[76]. Indeed, under the condition (5) the current between layers cannot destroy the superconductivity inside the layers, and the current density $j_{n,n+1}$ between the layers n and n + 1 can be calculated by perturbation theory under the assumption that the order parameters of the layers Δ_n and Δ_{n+1} are

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specified.[8] Just as in the case of ordinary Josephson junctions, the current $j_{n,n+1}$ is determined in this situation by the formula

$$j_{n,n+1} = j_c(\Delta) \sin(\varphi_n - \varphi_{n+1}), \qquad (6)$$

where φ_n is the phase of the order parameter in the layer n. We note that for Josephson effects to appear in ordinary tunnel junctions it is necessary that the probability of the passage of the electron through the barrier at the junction be much less than unity.[77] For a Josephson interaction of the layers to appear in layered compounds we need the stronger condition (5). The reason is in ordinary Josephson junctions between bulky metals the superconductivity is a volume effect, and it is stronger than the surface effect of electron tunneling between superconductors. In layered compounds, the difference of the layers is essentially atomic, and both effects (superconductivity and tunneling) have the same dimensionality.

Let us see now in which layered compound is the condition (5) satisfied. If d is the distance between the conducting layers, then the quantity $\tau_\perp^{-1}$ is connected with the diffusion coefficient $D_\perp$, the conductivity $\sigma_\perp$, and the coefficient γ in the electronic thermal conductivity by the relations (2) and

$$\sigma_\perp = e^2 D_\perp N(0), \quad D_\perp = d^2 \tau_\perp^{-1}. \qquad (7)$$

Using the data of Table I we can now estimate the quantities $\hbar/\tau_1$ at low temperatures (T < 10°K). For $TaS_2(Py)_{1/2}$ at $\sigma_\perp = 0.5 \ \Omega^{-1} \ cm^{-1}$ we obtain $\hbar/\tau_1 \approx 0.03°$K, and the condition (4) is satisfied practically everywhere below T_c. In $4Hb-TaS_2$ we have $\hbar/\tau \approx 10°$K and at $T \ll T_c$ an intermediate case $\hbar/\tau_\perp \approx \Delta$ is realized. In TaS_2 and $NbSe_2$ we are dealing with ordinary anisotropic superconductivity, since $\hbar/\tau_1 \approx 10^2 - 10^{3°}$K.

B. Differential-Difference Ginzburg-Landau Equations for Quasi-Two-dimensional Superconductors

In Sec. A of Chap. 7 it will be shown that a superconducting long-range order exists below T_c in quasi-two-dimensional systems to which ordinary superconductivity theory, particularly the BCS theory, is applicable. However, layered superconductors have under the condition (5) a number of peculiarities similar to those observed in Josephson junctions. These peculiarities must manifest themselves already at temperatures near T_c (in the region where $\hbar/\tau_\perp \ll \Delta^2(T)/T_c \ll \Delta(0)$), and they can be described with the aid of the Ginzburg-Landau equations for the order parameter. To derive these equations from the general equations of the BCS theory we use Gor'kov's usual procedure.[78] The Ginzburg-Landau equation terms that are linear in Δ are obtained from the integral equation for the order parameter $\Delta(\mathbf{r})$ (see e.g., Chap. 5 of the book[79])

$$\Delta(\mathbf{r}) = \int \lambda(\mathbf{r}') K(\mathbf{r}, \mathbf{r}') \Delta(\mathbf{r}') d\mathbf{r}', \quad \omega = 2\pi T\left(n + \frac{1}{2}\right),$$
$$K(\mathbf{r}, \mathbf{r}') = \sum_\omega G(\omega, \mathbf{r}, \mathbf{r}') G(-\omega, \mathbf{r}, \mathbf{r}'), \qquad (8)$$

where $G(\omega, \mathbf{r}, \mathbf{r}')$ is the one-electron temperature Green's function in the "frequency" representation, and

$\lambda(\mathbf{r}')$ is the parameter of the attraction of the electrons due to their interaction with the phonons. In ordinary isotropic metals, the electron density is practically constant in space, and in the absence of an external field $\lambda K(\mathbf{r}, \mathbf{r}')$ is a difference kernel, and Δ is independent of $\mathbf{r}$. In layered and especially in intercalated compounds, the electron density (like the order parameter) is concentrated mainly in the conducting layers, and the kernel $\lambda(\mathbf{r}')K(\mathbf{r}, \mathbf{r}')$ is not of the difference-type in the coordinates z and z' even in the absence of an external field. However, the equations of the BCS theory can be greatly simplified for such systems by confining oneself to a description of the superconductivity inside the conducting layers, and disregarding the regions where the electron density is low (it is precisely just such a description which is used for the Josephson junctions). The changeover to such a treatment is effected by changing from the continuous coordinate representation $\mathbf{r} = (\boldsymbol{\rho}, z)$ to the Wannier representation $(\boldsymbol{\rho}, n)$ with respect to the coordinate z. With such a change, the electron motion along and across the layer can be regarded as independent, and the discrete variable n indicates the number of the layer. The order parameter in the Wannier representation is expressed in terms of the function $\Delta(\mathbf{r})$ with the aid of the relation

$$\Delta_{n_1 n_2}(\rho) = \int_{-\infty}^{+\infty} \Delta(\rho, z) w_{n_1}(z) w_{n_2}(z) dz, \qquad (9)$$

where $w_n(z)$ is the Wannier function of the layer n. In (9) and in the corresponding equations for Δ we need retain only the terms that do not contain integration with respect to the Wannier functions of different layers (the terms discarded in this case are small to the extent that the ratio $\epsilon_\perp/\epsilon_F$ is small). Equations (8) then takes the form

$$\Delta_n(\rho) = \Lambda \sum_{n'} \int_{-\infty}^{+\infty} d\rho' K_{n,n'}(\rho - \rho') \Delta_{n'}(\rho'), \quad \Lambda = \int_{-\infty}^{+\infty} \lambda(z) |w_n(z)|^4 dz = \frac{\bar\lambda}{d_0}, \qquad (10)$$

where $\bar\lambda$ is the average value of the interaction over a conducting layer of thickness d_0. Now $K_{n,n'}$ is a difference kernel with respect to the discrete variables n and n' by virtue of the translational symmetry along the z axis. The off-diagonal elements of $K_{0,n}$ are smaller at $\epsilon_\perp \ll T_c$ than the diagonal element $K_{0,0}$, to the extent that $(\epsilon/T_c)^n$ in the case of diffusion (hopping) of the electrons between the layers.[75] We can therefore retain in the integro-difference equation (10) only the nearest-layer interaction. At $\tau = (T - T_c)/T_c \ll 1$ we can obtain from (10) for the Ginzburg-Landau order parameter an equation that is differential in ρ and of the difference type in n. Indeed, the characteristic length of the kernel K along the layer is the correlation length ξ_0. At $\tau \ll 1$, the order parameter will change over a length $\xi(T) = \xi_0/\sqrt{\tau}$ along the layer, and at $\xi(T) \gg \xi_0$ Eq. (10) which is integral in ρ can be replaced by a differential equation.

Let us consider next the case when the superconductor inside the layer is isotropic and pure (mean free path in the layer $l_\parallel \gg \xi_0$), and let us introduce the Ginzburg-Landau parameter $\psi_n = \sqrt{7\zeta(3)} N \Delta_n/4\pi T_c$ ($\zeta(x)$ is the Riemann function). Adding to (10) terms of third order in ψ_n and introducing in gauge-invariant fashion the vector potential $\mathbf{A}$, we obtain

$$\left[\frac{\hbar^2}{4m_\parallel}\left(-i\frac{\partial}{\partial\rho} - \frac{2e}{\hbar c}\mathbf{A}\right)^2 + \frac{1}{\eta}\left(-\tau + \frac{2d_0}{Nd}|\psi_n|^2\right)\right]\psi_n$$
$$+ \frac{t}{\eta}(2\psi_n - \psi_{n+1}e^{-i\chi_n} - \psi_{n-1}e^{i\chi_n}) = 0, \quad \mathbf{A} = (A_x, A_y),$$
$$\chi_n = \frac{2e}{\hbar c}\int_{nd}^{(n+1)d} A_z \, dz, \quad \eta = \frac{7\zeta(3)\,\epsilon_F}{(2\pi T_c)^2}, \quad t = \frac{\pi\hbar}{8\tau_\perp T_c}. \qquad (11)$$

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[8] In a purely two-dimensional system, the phase fluctuations destroy the long-range superconducting order. However, the transitions of the electrons between the layers suppress these fluctuations completely and the order parameter inside the layer is practically independent of the probability of electron transitions between the layers. This question is considered in greater detail in Sec. a of Chap. 7.

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For the current density $j_n(\rho)$ inside the layer n and for the current density $j_z(n, n+1)$ between the layers n and $n+1$ we obtain

$$j_n(\rho) = -\frac{ieh}{2m_{\parallel}}\left(\psi_n^* \frac{\partial}{\partial\rho}\psi_n - \psi_n \frac{\partial}{\partial\rho}\psi_n^*\right) - \frac{2e^2}{mc}A(n)|\psi_n|^2, \quad (12a)$$

$$j_z(n, n+1) = -\frac{2ietd}{\hbar\eta}[\psi_n^*\psi_{n+1}e^{-i\chi_n} - \psi_n\psi_{n+1}^*e^{i\chi_n}]. \quad (12b)$$

In the case of band motion of the electrons between the layers ($l_\perp \gg d$) and the electron spectrum is of the form

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2}{2m}(k_x^2 + k_y^2) + 2b(1 - \cos k_z d), \quad 0 \leqslant k_z d \leqslant 2\pi, \quad (13)$$

the Josephson interaction of the layers is realized if[9] $b \ll \Delta(T)$. At $b \ll T_c$ we obtain $t = 7\zeta(3)(b/8\pi T_c)^2$ and $\eta = 7\zeta(3)\,\epsilon_F/(4\pi T_c)^2$. In this model, Eqs. (11) and (12) can be obtained in exactly the same manner as the equations that are obtained for the Josephson junctions in the tunnel-Hamiltonian model.[77] Equations (11) and (12) were first derived by Lawrence and Doniach[76] by just this method.

Equation (12b), which is valid at $\tau \ll 1$, is equivalent to Eq. (6) with $j_c = etd^2N\tau/\hbar\eta d_0$. However, physically Eq. (6) for the current between the layers is valid for all temperatures and $j_c = etd^2N_s/2\hbar\eta d_0$, where N_s is the number of "superconducting" electrons at the given temperature.[78]

It follows from (10) that at $\hbar/\tau_\perp \ll T_c$ the BCS formula for T_c of layered superconductors is given by

$$T_c \approx \hbar\omega_D \exp\left(-\frac{1}{g}\right), \quad g = \Lambda N_2(0) = \bar{\lambda}N_2(0)d_0^{-1}, \quad (14)$$

where $N_2(0)$ is the two-dimensional density of states inside the layer, equal to $m_{\parallel}/2\pi\hbar^2$ in the isotropic case. In order of magnitude, the thickness d_0 of the conducting layer in dichalcogenides is of the order of 2 Å. It follows from (14) that intercalation (or pressure) changes T_c only to the extent that a change takes place in the characteristics of the conducting layer (Λ and $N_2(0)$), and these changes are usually small.[10] At the same time, all the thermodynamic and kinetic parameters of layered compounds (for example, the specific heat, the electric conductivity, etc.) are determined by the average density of states over the entire volume, which is equal to $m_{\parallel}/2\pi\hbar^2 d$ in the case of isotropic motion of the electrons in the layer. It also follows from (10) and (12) that T_c depends on the number of layers N in the crystal only to the extent to which the characteristics Λ and $N_2(0)$ vary inside the conducting layer as a result of the presence of the neighboring layers[11].

C. Josephson Effects in Quasi-Two-Dimensional Superconductors

Under conditions when the external fields cannot change the modulus of the order parameter in the layer (electric field perpendicular to the layers and magnetic field $H_{\parallel}$), there will be observed in quasi-two-dimen-

sional superconductors effects that are qualitatively similar to those characteristic of Josephson junctions. In essence, under condition (5) layered compounds are sets of parallel Josephson junctions with superconductors of atomic thickness, arranged in parallel. Therefore, at a constant potential difference U applied perpendicular to the layers, one can observe an alternating Josephson current at the frequency $\omega = 2eU/\hbar N$, where N is the number of layers between which the voltage U is applied.[75,82] In quasi-two-dimensional superconductors there should exist also natural oscillations corresponding to Josephson plasma oscillations.[76] In layered systems these effects become more complicated, however, by the fact that the external fields cannot be screened by one conducting layer of atomic thickness. The influence of this circumstance on nonstationary Josephson effects in an electric field in layered systems has not yet been investigated. On the other hand, the behavior of layered quasi-two-dimensional superconductors in a weak magnetic field $H_{\parallel}$ turns out, by virtue of this circumstance, to be quite unique and, in particular, the structure of the vortex in layered systems with $\epsilon_\perp \ll \Delta^2/T_c$ differs both from the structure of the Abrikosov vortex for isotropic type-II superconductors and from the structure of the vortex in ordinary Josephson junctions between two bulky superconductors[77] (see Sec. a of Chap. 8 below).

7. SUPERCONDUCTING FLUCTUATIONS IN QUASI-TWO-DIMENSIONAL SYSTEMS

A. Existence of Superconducting Long-Range Order

Rice[83] and Hohenberg[84] have shown that in one-dimensional and two-dimensional systems the existence of superconducting long-range order is impossible because of fluctuations.[12] This statement, however, does not hold for quasi-one-dimensional and quasi-two-dimensional systems. Dzyaloshinskiĭ and Kats[19,87] have shown that even a very weak overlap of the electron wave functions of neighboring layers suppresses the phase fluctuations that disturb the long-range order in a purely two-dimensional system. Indeed, let us estimate, following[68,87], that region near the critical temperature T_c (obtained in the self-consistent field approximation), in which the phase fluctuations alter significantly the results of the self-consistent-field approximation in which no account is taken of the fluctuations. Within the framework of the Ginzburg-Landau functional, the classical (thermal) fluctuations can be taken into account in the manner used by Rice.[83] We calculate the coordinate function of the Ginzburg-Landau order parameter $g_n(\rho) = \langle\psi_n^*(\rho)\psi_0(0)\rangle$[68,82,88], using a functional quadratic in $\psi_n(\rho)$ and corresponding to Eqs. (11), and neglecting the fluctuations of the modulus of the order parameter, which are insignificant in the quasi-two-dimensional case

$$\langle\psi_n^*(\rho)\psi_0(0)\rangle = \int \psi_n^*(\rho)\psi_0(0)e^{-F(\varphi_k(\rho))/T}D\varphi_k\left[\int e^{-F(\varphi_k(\rho))}D\varphi_k\right]^{-1},$$

$$F(\varphi_k(\rho)) = \psi_0^2\sum_k\left\{\frac{\hbar^2}{2m_{\parallel}}\left(\frac{\partial\varphi_k}{\partial\rho}\right)^2 + \frac{2t}{\eta}[1-\cos(\varphi_{k+1}-\varphi_k)]\right\}, \quad (15)$$

$$\psi_k(\rho) = \psi_0 e^{i\varphi_k(\rho)}, \quad \psi_0^2 = \frac{N\tau d}{2d_0}.$$

As a result, as $r \to \infty$, we obtain at $\epsilon_\perp \ll T_c$ ($t \ll 1$) for the quantity $g(\infty) = \lim g(r)$ that characterizes the long-range superconducting order[88,82] the expression

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[9] In practice, it appears that the case $l_\perp \gg d$ is impossible in the case $b \ll T_c$.

[10] The incorrect transition to a discrete representation in the BCS equations, used in [80], has led to the incorrect conclusion that $\Lambda \sim d^{-1}$ and that T_c therefore depends significantly on the distance between the conducting layers.

[11] No account was taken in [81] of the term $2t\psi_n/\eta$ in the left-hand side of (11), and dependence of T_c on the number of layers in the crystal was obtained in the form $T_c(N) = T_c(1)[1 + 2\eta t \cos(\pi/(N+1))]$. This conclusion is incorrect, so that it is impossible to explain the decrease of T_c in $NbSe_2$ with decreasing number of layers. [13b]

[12] Yet in two-dimensional systems the superconducting properties can manifest themselves also without realization of long-range order. [85,86]

$$g(\infty) = \psi_0^2 e^{-\mu}, \quad \mu = \frac{T}{\tau \varepsilon_F} |\ln t|. \quad (16)$$

It is seen from (16) that even at a very small value of t the fluctuations do not change the solution of the self-consistent field in the entire temperature region, with the exception of a very close vicinity of T_c (the critical region). It appears that allowance for the quantum fluctuations does not change significantly the estimate (16) (in quasi-one-dimensional systems, the estimate corresponding to (16) changes little after the quantum fluctuations are taken into account[89]).

Thus we can use the usual self-consistent-field method to describe quasi-two-dimensional superconductivity. Within the framework of this method, at $\epsilon_\perp \ll T_c - T$, the system of electrons can be regarded as two-dimensional if we consider those system characteristics which differ from zero as $\epsilon_\perp \to 0$ (such as T_c, H_{c2}, but not $H_{c1}(\parallel)$).

B. Superconducting Fluctuations Above T_c in Quasi-Two-Dimensional Systems

Although the transitions of the electrons between the layers suppress the order-parameter fluctuations, nonetheless the fluctuations in quasi-two-dimensional systems turn out to be stronger than in ordinary three-dimensional superconductors. Thus, for isotropic superconductors the quantity μ in (16) is of the order of $TT_c / \epsilon_F^2 \tau$,[90] and in these superconductors the region of noticeable fluctuations is much narrower than in quasi-two-dimensional systems. In fact, in layered superconductors with $\epsilon_\perp \ll T_c$ in the temperature region $T - T_c \gg \epsilon_\perp$ we can disregard the transitions of the electrons between the layers. Under the conditions we can use for the layered superconductors all the calculations of the fluctuation quantities which were obtained for pure two-dimensional systems. Near T_c (i.e., in the region $\epsilon_\perp \ll T - T_c < T_c$), the results obtained by the Ginzburg-Landau functional are valid, and they show that the fluctuation diamagnetic susceptibility $\chi_\perp$, which is perpendicular to the layers, together with the cc conductivity $\sigma_\parallel$ and the specific heat, increases as $T \to T_c$ in proportion[91, 92] to $\tau^{-1} = T_c / (T - T_c)$ (in the three-dimensional case $\chi \sim \tau^{-1/2}$). In the region $T - T_c \ll \epsilon_\perp$ the fluctuations acquire a three-dimensional character. The transition from the three-dimensional behavior with increasing temperature $T - T_c$ was calculated by Yamaji[93] within the framework of the Ginzburg-Landau functional corresponding to Eqs. (11).[13] In the region $T - T_c \ll T_c$, in the case of arbitrary $\beta = \hbar / \tau_\perp T_c$, we obtain the expression

$$\chi_\perp = -\frac{k_B T_c}{3\pi} \left(\frac{e}{\hbar c}\right)^2 \frac{\xi_{GL}^2(0)}{\sqrt{\tau((\pi^2 \beta/2) + \tau)}}, \quad \xi_{GL}^2 = -\frac{2e}{\hbar c} T_c \left(\frac{dH_{c2\perp}}{dT}\right)_{T_c}. \quad (17)$$

So far, only diamagnetic fluctuations in $TaS_2(Py)_{1/2}$ have been experimentally investigated[95, 96], and also fluctuations of microwave absorption in $2H-NbSe_2$.[97] For $NbSe_2$, according to the estimate of Sec. a of Chap. 6, the "dimensionality" parameter β is large (≈ 100) and accordingly the experimental results of[97] are described by the formula for the fluctuation microwave conductivity of a three-dimensional system[98] in a wider temperature interval than by the formula obtained for the two-dimensional case. In $TaS_2(Py)_{1/2}$, according to the estimates of Sec. a of Chap. 6, we can expect an almost two-dimensional behavior of the fluctuations. Indeed, it

was observed in[95] that above T_c the fluctuation susceptibility $\chi_\perp$ decreased very slowly with increasing temperature, and the relation $\chi_\perp \sim 1/T$ was satisfied in the temperature interval from 10 to 35°K. The corresponding diamagnetic moment $M_\perp$ did not vanish in magnetic fields exceeding $H_{c2\perp}(T = 0)$. The wide temperature region of the fluctuations and the independence of $M_\perp$ of H have cast doubts on the assumptions made in[95] that the diamagnetic moment observed by the authors is due only to superconducting fluctuations[20a]. Superconducting fluctuations of the diamagnetic moment near T_c can be measured more accurately, and this was done in[96]. Prober, Beasley, and Schwall observed a relation $\chi_\perp = a\tau^{-1}$ with $a = 2.5 \times 10^{-7}$ cm³/g, and according to the data of[20a] in this temperature region the corresponding diamagnetic moment decreased rapidly with increasing field H above $H_{c2\perp}(0)$. However, as shown by Gerhardts[80], the fact that $\chi \sim \tau^{-1}$ in some temperature region near T_c is by itself still not proof that the pure two-dimensional case is realized. Indeed, a region with such a dependence exists also in three-dimensional systems ($\beta \gg 1$), and with decreasing β it only broadens towards lower temperatures. The constant a is determined by the values of $\xi_{GL}(0)$ and β, and Gerhardts, taking $\xi_{GL}(0)$ from the data for $H_{c2}(\perp)$, obtained $\beta = 0.15$.

In the temperature region $T \gtrsim 1.5 T_c$ and in strong magnetic fields, calculations based on the use of the Ginzburg-Landau functional are no longer correct. Complete calculations for the diamagnetic fluctuation moment within the framework of the BCS theory and using the electronic spectrum (13) are contained in[80], for dirty superconductors and arbitrary β they are found in[99], for dirty superconductors with $\beta = 0$ in[100], and for pure superconductors at arbitrary β in[101]. It is shown in[100] that in the region above $2T_c$, in dirty layered superconductors with $\beta \ll 1$, the zero-point oscillations of the Cooper pairs become significant (these pairs are bosons and are present even at $T = 0$, owing to the zero-point oscillations). The diamagnetic susceptibility associated with these zero-point oscillations decreases slowly with increasing temperature, and the corresponding diamagnetic moment vanishes only in very strong fields.

For temperatures close to T_c, the contribution of the thermal fluctuations χ_T to the total fluctuation diamagnetic susceptibility χ greatly exceeds the contribution of the zero-point oscillations χ_0 (as $T \to T_c$ we obtain $\chi_T \sim (T - T_c)^{-1}$ and $\chi_0 \sim \ln(T - T_c)^{-1}$). Far from T_c, however, the situation changes, and at $T > 5T_c$ we have $\chi_0 \gtrsim \chi_T$ at parameter values close to the parameters of the crystals $TaS_2(Py)_{1/2}$. In this situation, the total diamagnetic susceptibility decreases with increasing temperature very slowly, remaining noticeable up to $10T_c$. Thus, in dirty quasi-two-dimensional superconductors one can observe in principle the picture of diamagnetic fluctuations which was observed in $TaS_2(Py)_{1/2}$ by the authors of[95]. As $T \to 0$, the zero-point oscillation leads to a suppression of the fluctuation diamagnetic moment and of the conductivity at $H > H_{c2}$, and this effect can be measured experimentally. No such measurements have been performed so far, however.

8. CRITICAL MAGNETIC FIELDS IN LAYERED SUPERCONDUCTORS

The features of the structure of layered superconductors become manifest most brightly in the anisotropy of their critical magnetic fields and currents. All the pres-

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[13]Analogous calculations for the conductivity in a magnetic field were made recently by Klemm[94].

ently known layered superconductors are type-II super-conductors. This is not an accident. Indeed, the correlation length $\xi_0 = \hbar v_F/\pi\Delta_0$ in layered superconductors is small because of the narrowness of the d bands. At the same time, the London depth of penetration even in a perpendicular field $\lambda_L(\parallel) = \sqrt{m_\parallel c^2/4\pi e^2 N_S}$ is large in these superconductors, owing to the large value of the effective mass $m_\parallel$ along the layers and to the small average electron density N. We consider first the behavior of layered superconductors in weak fields and determine the field H_{c1}, starting with which the magnetic field penetrates into the sample.

A. Critical Field H_{cl} and Vortex Structure

In anisotropic superconductors $NbSe_2$ and TaS_2, the quasi-two-dimensionality condition (5) is not satisfied, and the structure of the vortex in them remains qualitatively the same as in ordinary superconductors.[79] A normal state is realized in this case at the center of the vortex and the vortex differs from the case of an isotropic crystal only in that in the field $H_\parallel$ the boundaries of the normal-state region, and also the distribution of the field and of the currents, are elliptic.[76] The field H_{c1} is anisotropic, and

$$H_{c1}(\parallel) = \frac{\Phi_0}{4\pi\lambda_\perp\lambda_\parallel}\ln\sqrt{\frac{\lambda_\parallel\lambda_\perp}{\xi_\parallel\xi_\perp}}, \quad H_{c1}(\perp) = \frac{\Phi_0}{4\pi\lambda_\parallel^2}\ln\frac{\lambda_\parallel}{\xi_\parallel}, \quad \Phi_0 = \frac{\pi c\hbar}{e},$$

(18)

where $\lambda_\parallel$ and $(\lambda_\parallel\lambda_\perp)^{1/2}$ are the depths of penetration of the field perpendicular and parallel to the layers, and $\xi_\parallel$ and $\xi_\perp$ are the correlation lengths along and across the layer.

In quasi-two-dimensional superconductors, under condition (5), destruction of superconductivity inside the layer in a field $H_\parallel$ is impossible (Sec. a of Chap. 6), and the picture of the vortex in the field $H_\parallel$ becomes qualitatively different. The structure of the vortex can be obtained in this case with the aid of Maxwell's equations and the equation for the currents (12).[75] Calculation shows that everywhere except in the region of the vortex core, with dimensions on the order of d, the currents and the fields are weak and can be described within the framework of the approximation, linear in the field, for the current between the layers (12b). The distribution of the currents and of the field outside the core of the vortex is elliptic with characteristic dimensions $\lambda_\parallel$ and $\lambda_\perp$ across and along the layers. The value of $\lambda_\parallel$ is determined in the usual manner, and $\lambda_\perp = (c\Phi_0/8\pi^2 dj_c)^{1/2}$ $= (7\Phi_0^2\epsilon_F/\pi^4 d^2\Delta^2\beta N_S)^{1/2}$. The center of the vortex is in the space between the layers, and the currents between the layers reach their maximum value j_c in the region of the core of the vortex. The contribution of this region to the vortex energy is small (as in the usual case), and we obtain with logarithmic accuracy for $H_{c1}(\parallel)$ and $H_{c1}(\perp)$ the following expressions (the vortex in the field $H_\perp$ is ordinary)[14]

$$H_{c1}(\parallel) = \frac{\Phi_0}{4\pi\lambda_\parallel\lambda_\perp}\ln\frac{\lambda_\parallel}{d}, \quad H_{c1}(\perp) = \frac{\Phi_0}{4\pi\lambda_\parallel^2}\ln\frac{\lambda_\parallel}{\xi_\parallel}.$$

(19)

The static structure of the vortex state in weak fields remains the same in the quasi-two-dimensional case as in ordinary isotropic superconductors, if the length scales are suitably altered. However, the dynamics of the vortex motion and vortex oscillation change in the quasi-two-dimensional case in a field $H_\parallel$ and in a field

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[14]A solution for the vortex state in a field $H_\parallel$, obtained in [102], yields a larger value of $H_{cl}(\parallel)$.

TABLE V

Compound	T_c, °K	$\frac{dH_{c1(\perp)}}{dT}$, °/°K	$\frac{dH_{c2(\perp)}}{dT}$, °/°K	$\left(\frac{H_{c2\parallel}}{H_{c2\perp}}\right)^2_{T\to T_c}$	$H_{c2\parallel}(T)$ kOe	$H_{c2\parallel}(T)$ °K	H_p^*, kOe	References
2H-NbSe2	7; 7.38	47	6.4—7.9	10—12	130	1.2	129	35, 103, 104, 105
2H-TaS2	>1			45				
TaS2(Py)1/2	3.25		2.8—3.4	>2000	>150	1.4	60	105, 106
2H-NbS2	6.3		7.8	8.5			115	107

$H_\perp$ (in a field $H_\parallel$ there is no normal state inside the vortex, and in a field $H_\perp$ there is no continuous normal-state core, and vortices of different layers are coupled only by the magnetic field). As the temperature approaches T_c, the condition (5) ceases to hold and the inequality is reversed in the immediate vicinity of T_c. In this vicinity a normal state appears inside the vortex, and the critical fields $H_{c1}(\parallel, \perp)$ are determined by expressions (18).

Among the layered superconductors, the field H_{c1} was investigated so far experimentally only for $NbSe_2$ near T_c,[103], and we shall discuss these data later on together with the data for the field H_{c2}.

B. Upper Critical Field H_{c2} in $NbSe_2$ and the Effective-Mass Model

The data for the fields H_{c1} and H_{c2} in the superconductors $2H-TaS_2$, $2H-NbSe_2$, and $TaS_2(Py)_{1/2}$ are listed in Table V. Since the anisotropy in $2H-TaS_2$ and $2H-NbSe_2$ is not very strong (condition (5) is not satisfied), the behavior of these superconductors near T_c can be described within the framework of the Ginzburg-Landau equations with anisotropic "mass"[74,105,103,108]. In this model, the critical field H_{c1} is determined by expressions (18) with $\lambda_\perp = \lambda_\parallel/\alpha$, $\xi_\perp = \xi_\parallel\alpha$, $\alpha = (m_\parallel/m_\perp) = (m_\parallel/m_\perp)^{1/2}$ and $m_\parallel$—the effective "mass" for the motion of a pair inside the layer (the motion inside the layer will be regarded as isotropic), and $m_\perp$ is the "mass" for the motion of the pair in a direction perpendicular to the layers. The temperature dependences of the parameters λ and ξ, and also of the field $H_{c2}(\theta)$ (θ is the angle between the magnetic field and the plane of the layers) are given by

$$\lambda_{\perp,\parallel}(T) = \lambda_{\perp,\parallel}\left(1 - \frac{T}{T_c}\right)^{-1/2}, \quad \xi_{\perp,\parallel} = \xi_{\perp,\parallel}\left(1 - \frac{T}{T_c}\right)^{-1/2},$$

$$H_{c2}(\theta, T) = \frac{\Phi_0}{2\pi\xi_\parallel^2(T)\sqrt{\sin^2\theta + \alpha^2\cos^2\theta}}.$$

(20)

In $NbSe_2$, according to the data of[103], we have $\alpha = 0.3$, $\xi_\parallel = 71$ Å, and $\lambda_\parallel = 690$ Å. From the relations for the thermodynamic critical field H_{c0} at T = 0,

$$H_{c0} \approx \frac{\Phi_0}{4\pi\lambda_\parallel\xi_\parallel\sqrt{2}}, \quad H_{c0}^2 = 4\pi N(0)\Delta_0^2,$$

(21)

we obtain $N(0) \approx 10^{35}$ erg^{-1}cm^{-3}, which is approximately 2.5 times larger than $N(0)$ calculated from data on the coefficient γ in the specific heat.[31][15] Since no gap anisotropy was observed in $NbSe_2$, we can assume that the entire anisotropy of the motion of the electrons in this compound is due to anisotropy of the electron effective mass. Using then for the electron spectrum the expression

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[15]It is noted in [103] that this disparity can be due to the fact that measurements of the specific heat were carried out on powdered samples and more accurate measurements of γ on single crystals are needed.

$$\varepsilon(k) \approx \frac{\hbar^2}{2m_\parallel}(k_x^2 + k_y^2 + \alpha^2 k_z^2), \qquad (22)$$

we obtain for the density of states and for the Fermi level the relations

$$N(0) = \frac{m_\parallel}{2\pi\hbar^2}\left(\frac{3N}{\alpha^2\pi}\right)^{1/3}, \quad \varepsilon_F = \frac{3N}{4N(0)}. \qquad (23)$$

Knowing α, N, N(0), and $\sigma_\parallel$ we can calculate the parameters $\lambda_\parallel$ and $\xi_\parallel$ and compare them with the values obtained from experiment. At $N(0) = 1.0 \times 10^{35}$ erg^{-1}cm^{-3} it follows from (23) that $m_\parallel = 13.5 m_e$ (for NbSe$_2$ the optical mass is $m_\parallel = 9.7 m_e$), $\varepsilon_F \approx 0.07$ eV, $\xi_{0\parallel} = \hbar v_{F\parallel}/\pi\Delta_0 \approx 80$ Å, and $\lambda_{L\parallel}0 = \sqrt{3c^2/8\pi N(0)v_{F\parallel}^2 e^2}$ = 1600 Å. Using the values of the conductivity from Table I and relations of the type (7) with $D_{\perp,\parallel} = v_{F\perp,\parallel}l_{\perp,\parallel}/3$, we obtain $l_\parallel \approx (70-250)$ Å and $l_\parallel = (2-4)l_\perp$. These estimates show that in NbSe$_2$ there is realized the case of intermediate purity, when $\xi \approx l$. The values of $\xi_{0\parallel}$ and $\lambda_{L\parallel}$ presented above yield $\xi_\parallel \approx 60$ Å and $\lambda_\parallel \approx 1100$ Å. The obtained values of $\xi_{0\parallel}$ and $\lambda_{L\parallel}$ differ from the experimental data by more than two times, and the model of the anisotropic effective mass of the electron (elliptic Fermi surface) must be regarded as satisfactory.

We consider now the data for the upper critical field at low temperatures. Figure 11 shows the temperature dependence of $H_{c2\parallel}$ and $H_{c2\perp}$ in NbSe$_2$ as measured by Foner and McNiff[104]. The experimental points for both $H_{c2(\parallel)}$ and $H_{c2\perp}$ from these data and from the data of [103] lie above the calculated curve at low temperatures. This excess is not very large, and it may be due to the difference between the true Fermi surface and an elliptic one. The most surprising circumstance is, however, that in NbSe$_2$ we do not see any decrease of $H_{c2(\parallel)}$ due to the paramagnetic effect. Yet for singlet pairing of Cooper pairs under ordinary conditions, the superconductivity is destroyed only by the action of the paramagnetic effect at T = 0 in magnetic fields $H \geq H_p^* = \Delta_0/\mu_B\sqrt{2}$.[79] In NbSe$_2$ we obtain $H_p^* = 130$ kOe, and the joint action of the orbital and paramagnetic effect should lead at low temperatures to values $H_{c2(\parallel)}$, approximately 1.5–2 times lower than the experimental ones. Inasmuch as in NbSe$_2$ we see the action of only the orbital effect, it must be admitted that in this compound the paramagnetic effect turns out to be suppressed. The situation in TaS$_2$(Py)$_{1/2}$ in this respect is analogous, and we shall discuss the possible causes of the suppression of the paramagnetic effect in layered compounds later on, after we consider the experimental data for TaS$_2$(Py)$_{1/2}$.

C. The Field H_{c2} in TaS$_2$(Py)$_{1/2}$ and the Model of Quasi-Two-Dimensional Superconductors

According to estimates from the data on the conductivity and specific heat, the "dimensionality" parameter β in TaS$_2$(Py)$_{1/2}$ is approximately 0.01 (Sec. a of Chap. 6), while data on fluctuations (Sec. b of Chap. 7) yield $\beta \approx 0.15$. To describe the properties of this compound we can therefore use the model of quasi-two-dimensional superconductivity. If we assume that the electron motion inside the layer is isotropic and can be described by an effective mass $m_\parallel$, then $m_\parallel$ and ε_F can be determined from the relations

$$N(0) = \frac{m_\parallel}{2\pi\hbar^2 d}, \quad \varepsilon_F = \frac{N}{2N(0)}. \qquad (24)$$

From the data of Table I we obtain $N(0) \approx 10^{34}$ erg^{-1}cm^{-3}, $\varepsilon_F \approx 0.25$ eV, $m_\parallel \approx 9m_e$, $\xi_{0\parallel} \approx 3.5 \times 10^6$ cm, and $l_\parallel = (0.7-4) \times 10^6$ cm. According to measurements of $H_{c2\perp}(T)$

near T_c (see Table V) we have $\xi_\parallel = 1.1 \times 10^{-6}$ cm, and the model of quasi-two-dimensional superconductivity with isotropic motion of the electrons in a layer yields a fair estimate of the correlation length in TaS$_2$(Py)$_{1/2}$. In this compound, however, just as in NbSe$_2$, the values of $H_{c2}(\perp)$ at low temperatures, obtained by measuring microwave absorption,[106] lie above the curve calculated in the isotropic model or in the model of the quasi-two-dimensional superconductor with isotropic motion of the electrons in the layer.[75] In TaS$_2$(Py)$_{1/2}$, this disparity is even stronger than in NbSe$_2$, and the quantity (dH$_{c2\perp}$/dT) for this compound becomes positive at low temperatures in accordance with the data of [106]. According to the ideas concerning the structural transitions (Chap. 4) in layered compounds, the Fermi surface in the (k_x, k_y) plane should differ from a circle. Indeed in high-temperature phases of these compounds there should exist on the Fermi surface flat sections that are closed by the energy gap if a structure transition takes place. It is natural to assume that it is precisely these circumstances that lead to the unusual dependence of $H_{c2}(\perp)$ on T in TaS$_2$(Py)$_{1/2}$ and NbSe$_2$. We note, in contrast to the isotropic superconductors and NbSe$_2$ crystals, in the intercalated compound TaS$_2$(Py)$_{1/2}$ the transition in the field $H_{c2}(\perp)$ is, in accordance with the data of [106], greatly smeared out over the field at low temperatures. The reason for this effect still remains unclear.

On the basis of the obtained values of $m_\parallel$, ε_F, and β in TaS$_2$(Py)$_{1/2}$ we can estimate the value of the field H_{c1} and the depth of penetration λ. For crystals with $\xi_{0\parallel} \approx l_\parallel$ we obtain at $\lambda_\parallel \approx \lambda_{L\parallel} \approx 1300$ Å, $H_{c1}(\perp) \approx 300$ Oe and $\lambda_\perp \approx 0.1$ mm, $H_{c1}(\parallel) \approx 0.03$ Oe at $\beta = 0.1$ and $\lambda_\perp \approx 0.3$ mm, $H_{c1}(\parallel) \approx 0.1$ Oe at $\beta = 0.01$. In accordance with the estimates for $\lambda_\perp$, the experimental data[96] on the Meissner effect in TaS$_2$(Py)$_{1/2}$ show that $\lambda_\perp \gtrsim 0.5$ mm at low temperatures.

We consider now the data concerning the $H_{c2\perp}(T)$ dependence in TaS$_2$(Py)$_{1/2}$. Figure 12 shows the superconducting transition in a magnetic field at 1.4°K in one of the crystals of this compound.[105] At angles less than 10° between the magnetic field and the plane of the layer, the field is $H_{c2}(\theta) \approx H_{c2}(\perp)/\sin\theta$. At smaller angles the resistance does not reach the value characteristic of the

FIG. 11. Critical field H_{c2} (1) and H_{cs} (2) vs. temperature for single-crystal NbSe$_2$. The solid (dashed) curve shows the calculated H_{c2}(T) for a "dirty" (pure) isotropic superconductor of type II without allowance for the paramagnetic effect. The insert shows the radio-frequency losses (or the dc resistance) of functions of the applied field, and the method of determining H_{c2} and H_{cs}. [104]
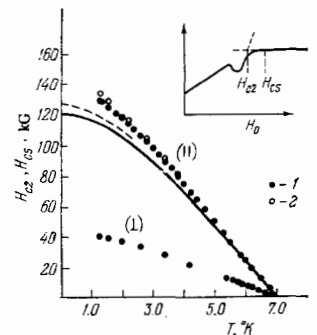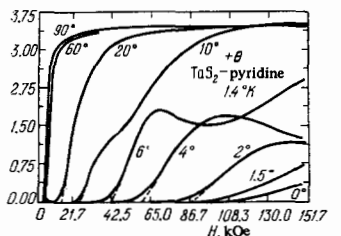
FIG. 12. Resistance (in arbitrary units) as a function of the magnitude and direction of the magnetic field in TaS$_2$(Py)$_{1/2}$ at 1.4°K. The angle indicates the direction of the field relative to the plane of the crystal layers. [105]

normal state, even in a field 150 kOe, and at $\theta = 0$ the growth of the resistance is not noticeable in fields up to 150 kOe, i.e., $H_{c2}(\|)$ in $TaS_2(Py)_{1/2}$ at $1.4°K$ exceeds 150 kOe and at $2.86°K$ we have in accordance with the data of [105] $H_{c2}(\|) > 84$ kOe. [16] For this compound, the paramagnetic limit is $H_p^* = 60$ kOe, and this limit is exceeded thus by more than 2.5 times.

D. Reasons for the Absence of an Orbital Effect for the Field H in Quasi-Two-Dimensional Superconductors

Within the framework of the concept of quasi-two-dimensional superconductivity in $TaS_2(Py)_{1/2}$ it is easy to understand why the orbital effect becomes ineffective in a field $H_\|$ at low temperatures. Indeed, in a strictly parallel field the orbital effect is limited by the Josephson currents between the layers. These currents, under the condition (5), cannot destroy the superconductivity. Only in the immediate vicinity of T_c is the condition (5) violated, and when the inverse inequality is satisfied, the superconductivity-destruction mechanism due to the orbital effect becomes the ordinary one. The transition from the ordinary behavior to the quasi-two-dimensional behavior in a magnetic field $H_\|$ at temperatures $T_c - T \ll T_c$ can be described with the aid of Ginzburg-Landau differential-difference equations of the type (11). [75,102,109,110] Choosing the potential A in the form $A_x = A_y = 0$, $A_z = Hy$, we obtain for the order parameter $\psi(y)$ the Mathieu equation

$$\left[\xi_0^2 \frac{d^2}{dy^2} - 2t \left(1 - \cos\frac{2edHy}{c\hbar} \right) - \tau \right] \psi(y) = 0, \qquad (25)$$

from which $H_{c2}(\|)$ is determined as that maximum value of H at which (25) has a nontrivial solution. At $T_c - T \ll tT_c$ we obtain the usual dependence of $H_{c2}(\|)$ on $T_c - T$:

$$H_{c2}(\|) = \frac{c\hbar\,[1 - (T/T_c)]}{2ed\xi_0\sqrt{t}}. \qquad (26)$$

However, as τ approaches $2t$, the field $H_{c2}(\|)$ increases without limit (if superconductivity-suppression mechanisms other than the orbital effect are disregarded):

$$H_{c2}(\|) = \frac{c\hbar}{2ed\xi_0\sqrt{2 - (\tau/t)}}. \qquad (27)$$

In $TaS_2(Py)_{1/2}$, measurements of $H_{c2}(\|)$ near T_c have not been performed, but a similar dependence was indeed observed in the crystals $Cs_{0.3}MoS_2$ and $Sr_{0.2}MoS_2$ in fields up to 36 kOe. [111] At present it is not clear, however, whether these results are due to crystal structure defects or are a reflection of the internal anisotropic motion of the electrons in the intercalated MoS_2 compounds. Thus, only the paramagnetic effect can lead to the destruction of superconductivity in a field $H_\|$ at $T < T_c(1 - 2t)$ in quasi-two-dimensional superconductors (see Note 4 added in proof at the end of the article).

E. Possible Causes of Suppression of Paramagnetic Effects in Layered Superconductors

In principle, the suppression of the paramagnetic effect in layered superconductors can be due to realization in these superconductors of an inhomogeneous state [75,112] by triplet pairing of the electrons from neighboring layers [113] and by spin-orbit scattering by

impurities [75,110]. However, the inhomogeneous state and the pairing of the electrons of the neighboring layers are sensitive to the scattering of electrons by impurities inside the layers, and they are destroyed if the electron mean free path inside the layer is $l \lesssim \xi_0$. [17] Yet according to the estimates obtained above the ratio $\xi_{0\|}/l_\|$ lies in the interval from 1 to 6 for different crystals $TaS_2(Py)_{1/2}$ and $NbSe_2$, and no dependence of $H_{c2}(\|)$ on the degree of purity of the samples has been observed in experiment. The spin-orbit scattering leads to an appreciable suppression of the paramagnetic effect if the electron with change of spin has a mean free path $l_{s0} \ll \xi_0$. [75,110] Since $l_{s0}/l \lesssim 10^{-2}$, the inequality $l_{s0} \gg \xi_0$ is satisfied in layered superconductors, and the spin-orbit scattering changes the paramagnetic limit insignificantly. In addition, in this case, too, there would be observed a strong sensitivity of $H_{c2}(\|)$ to the degree of purity of the crystals.

It is shown in [114] that suppression of the paramagnetic effect for the field $H_\|$ can be attributed to spin-orbit interaction of the conduction electrons in layered crystals with symmetry that admits of the existence of a polar vector (in pyroelectric crystals). There are certain grounds for assuming such a lattice symmetry for layered superconductors. The high-temperature 2H modifications of TaS_2 and $NbSe_2$ have inversion centers. It is not excluded, however, that in structure transitions appearance of a charge-density wave is accompanied by a a preferred direction in the lattice, and the symmetry center is lost (for example, in the case when the charge-density wave is not commensurate with the period of the initial lattice). Intercalation of TaS_2 crystals with pyridine suppresses the structural transition, but the pyridine molecules lower the lattice symmetry because the dimension of the molecule are not commensurate with the lattice period of TaS_2 in the layer (see Note 2 added in proof at the end of the article).

In addition to the suppression of the paramagnetic effect for the field $H_{c2}(\|)$, the spin-orbit interaction in pyroelectric layered crystals causes also the paramagnetic susceptibility in the superconducting state $\chi_s(\|)$ to approach the susceptibility of the normal state $\chi_n(\|)$. [114,115] At a perpendicular field direction, both effects turn out to be weaker. Therefore the correctness of the assumption of [114] can be verified by measuring the anisotropy of the Knight shift in layered superconductors. In a certain sense these measurements replace the measurements of the anisotropy of the paramagnetic limit H_p, since the quantities χ_n, χ_s and H_p are connected at $T = 0$ by the relation

$$\frac{1}{2}(\chi_n - \chi_s) H_p^2 = N(0)\,\Delta_0^2 \qquad (28)$$

(H_p is the paramagnetic limit with allowance for the spin-orbit effects).

9. CONCLUSION

We note now the most important experimental results which have been obtained to date for layered compounds and which determine at present the most important trends of future research in this field.

a) Measurements of the conductivity in a direction perpendicular to the layers, and investigations of the diamagnetic fluctuations at temperatures above T_c in

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[16] The surfaces of the TaS_2 layers in the $TaS_2(Py)_{1/2}$ obtained to date were not flat but wavy. Therefore at small angles θ there are always sections of TaS_2 layers that are parallel to the field, and in these sections the superconductivity is not destroyed at $H < H_{c2}(\|)$.

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[17] See Note 5 added in proof at the end of the article.

TaS$_2$(Py)$_{1/2}$, show that the motion of the electrons in this intercalated compound is very close to two-dimensional. According to estimates from data for the diamagnetic fluctuations in TaS$_2$(Py)$_{1/2}$, the parameter of the "dimensionality of electron motion" for the superconductivity is $\beta \approx 0.15$, while the data for the transverse conductivity yield $\beta \approx 0.01$. Although these two estimates undoubtedly are approximate, they show that the situation even in these intercalated crystals is close to that when the layer interaction becomes of the Josephson type.

b) Structural transitions with formation of charge-density wave, accompanied by an alteration of the Fermi surface, were observed in layered compounds. Even now, the experimental investigations show that a connection exists between these transitions and the superconducting properties.

c) In layered superconductors, the upper critical magnetic field parallel to the layers greatly exceeds the paramagnetic limit, and this effect cannot be explained within the framework of the spin-orbit scattering concepts customarily resorted to to explain the analogous phenomenon in isotropic or weakly isotropic crystals.

In conclusion, we list those trends of research on layered compounds which are presently most important and interesting for physics and for practical applications:

1) The presently existing experimental results and theoretical premises show that in TaS$_2$(Py)$_{1/2}$, or in intercalated compounds with even larger distances between the conducting dichalcogenide layers, it is possible in principle to observe the nonstationary Josephson effect. The imperfection of the crystal is for the time being still difficult hindering experiments of this type. However, even now certain ways of obtaining more perfect intercalated crystals have been found.[116] We note that a more accurate determination of the "electron motion dimensionality" parameter β might be obtained from measurements of the field $H_{c1}(\|)$ or of the field penetration depths $\lambda_\|$ and $\lambda_\perp$.

2) The character of the structure transitions in the 2H modifications of TaS$_2$ and NbSe$_2$, and the influence exerted by these transitions on the superconducting properties are presently one of the central problems in the physics of layered metals. In essence, in accordance with the assumption of[114], these can be ferroelectric transitions. The determination of the lattice structure in the low-temperature modifications is therefore a very important factor for verifying this premise. Measurements of the Knight-shift anisotropy in layered superconductors could provide an additional verification of the hypothesis that the lattices of layered metal TaS$_2$(Py)$_{1/2}$ and of the low-temperature modification of 2H–NbSe$_2$ are pyroelectric.

3) Layered intercalated superconductors afford a unique possibility of experimentally investigating the contribution of the zero-point oscillations of Cooper pairs to diamagnetism (and possibly) the conductivity of superconductors at temperatures $T \ll T_c$ and $H > H_{c2}$.

4) Great interest attaches to experimental work on the development of new intercalated layered crystals and crystals with alternating metallic and semiconducting layers. It appears that in principle it is possible to intercalate layered crystals with radical molecules. In this way it would be possible to obtain crystals in which the metallic layers alternate with ferromagnetic or anti-

ferromagnetic molecular layers. The coexistence of magnetic order and quasi-two-dimensional superconductivity in these systems could lead to interesting Josephson properties of such crystals[18] (see Note 6 added in proof at the end of the article).

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[18]See [117] in connection with this remark

Notes added in proof. 1) (See p. 520). In the review [118] are given detailed data on the observation of the superstructure (charge-density wave) in layered compounds. In modifications, the superstructure exists at all temperatures at which the research was performed. First-order transitions between polytypes of this modification correspond to changes of the superstructure. In 2H modifications, the superstructure appears below the temperature T_d.

2) (See p. 521). According to data on neutron scattering [119], a superstructure appears in 2H–TaSe$_2$ and 2H–NbSe$_2$ below T_d. This superstructure has a period that is not commensurate with the period of the initial lattice, but is close to triple the period of the initial hexagonal lattice. In both compounds, the period of the superstructure continuously changes with decreasing temperature, approaching the triple period. In 2H–TaSe$_2$ at 90°K, the period of the superstructure changes jumpwise, and below 90°K it is exactly equal to triple the period of the initial lattice. In 2H–NbSe$_2$, the periods remain noncommensurate down to 5°K. According to measurements of the elasticity of the crystals [20], the transition to a commensurate structure in 2H–NbSe$_2$ is not observed down to 1.3°K. The character of the restructuring of the Fermi surface due to the appearance of the superstructure is considered theoretically in [121,122].

3) (See p. 522). Intercalation of 2H–TaS$_2$ with hydrogen also raises T_d from 0.8 to 4.2°K, and the addition of hydrogen leads to a lowering of the maximum in the temperature dependence of the magnetic susceptibility. [123]

4) (See p. 529). According to [124], the upper critical magnetic field in compounds of MoS$_2$ with K, Rb, and Cs exceeds the paramagnetic limit, and the angular dependence of H_{c2} can be described within the framework of the model of the Josephson interaction of the layers.

5) (See p. 539). The authors of [112] have neglected the orbital effect and considered an inhomogeneous state, in which the order parameter varied in a direction perpendicular to the layers. Such an analysis is inconsistent, since the increase of H_{c2} through realization of an inhomogeneous state is possible in this case only in the case of a sufficiently strong interaction of the layers (at $\epsilon_\perp \gg \Delta^2/T_c$). But in this situation one cannot neglect the orbital effect. The order parameter must therefore vary in the plane of the layers in quasi-one-dimensional superconductors ($\epsilon_\perp \ll \Delta^2/T_c$) in the inhomogeneous state. [75]

6) (See p. 530). Intercalation of TaS$_2$ crystals with chromocene molecules Cr(C$_5$H$_5$) is reported in [125]. The obtained crystals are superconducting ($T_c = 2.9°K$) and paramagnetic below T_c, i.e., the superconducting layers in them are separated by layers of paramagnetic molecules.

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