Superconductivity in crystals without symmetry centers

L. N. Bulaevskiĭ, A. A. Guseĭnov, and A. I. Rusinov

P. N. Lebedev Physics Institute, USSR Academy of Sciences
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We consider the effect of spin-orbit interaction on the paramagnetic properties of superconducting crystals having a lattice without symmetry center. Systems of this type include superconducting metals with polar-symmetry lattice V_2Hf and VRu. Arguments are advanced favoring the assumption that there may be no symmetry center in a lattice of layered dichalcogenide metals with incommensurate charge-density wave or of intercalated layered metals. The paramagnetic susceptibility and the paramagnetic limit H_{ps} of the upper critical magnetic field are obtained for such superconductors as functions of the relative spin-orbit interaction $\alpha = \epsilon_1/\Delta(0)$, of the degree of purity of the crystals $\lambda = 1/2\tau\Delta(0)$, of the temperature, and of the field direction. The quantities χ and H_{ps} are anisotropic, and H_{ps} can greatly exceed the Chandrasekhar-Clogston paramagnetic limit H_p. The experimental data for H_{c2} in $2H-NbSe_2$ and $TaS_2(Py)_{1/2}$ are discussed from the point of view of the results.

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INTRODUCTION

We show in this article that the paramagnetic properties of a superconductor with a lattice having no symmetry center depend significantly on the spin-orbit interaction of the conduction electrons. In contrast to the compounds with spin-orbit scattering of electrons by impurities, [1,2] in a superconductor without a symmetry center this dependence turns out to be anisotropic, and manifests itself in first-order perturbation theory in the spin-orbit interaction. In a number of cases (pure superconductors, superconductors made up of light elements), the interaction considered by us seems therefore to be the only mechanism capable of changing the paramagnetic properties of an ordinary superconductor (the Chandrasekhar–Clogston limit for the upper critical magnetic field $H_p = \Delta(0)\sqrt{2}/g\mu_B$ at a temperature $T = 0$ and the vanishing of the paramagnetic susceptibility χ as $T \to 0$).

Consideration of superconductors whose lattices have no symmetry center is timely because superconducting metals with a lattice having a polar symmetry group are already known at present. [3] Such crystals include the compounds V_2Hf[4] (symmetry group C_{2v}^{20}, critical temperature $T_c = 8.7\,^\circ K$) and VRu[5] (symmetry group C_{4v}^1 and $T_c = 1.07\,^\circ K$). In addition, we present below considerations that suggest that in layered metals of the type $2H$-$NbSe_2$ ($T_c = 7.4\,^\circ K$) the transition to a state with incommensurate charge-density wave at $35\,^\circ K$[6,7] leads to a loss of the symmetry center of the lattice, although the high-temperature phase with hexagonal lattice does have such a symmetry. In principle, the appearance of a lattice without a symmetry center can result also from intercalation of layered metals by molecules that lower the symmetry of the lattice because their dimensions are not commensurate with the period of the initial lattice of the layered crystals. [8]

In Sec. 1 we consider the theory of spin-orbit interaction in crystals of the pyroelectric class in layered compounds with incommensurate charge-density wave. We calculate for such systems, on the basis of the Gor'kov equations with allowance for the scattering by the impurities, the paramagnetic susceptibility of the superconducting state (Sec. 2) and the paramagnetic limit for the upper critical magnetic field H_{ps} (Sec. 3). In Sec. 4, on the basis of the results, we discuss the possibility of explaining the experimental data for the upper critical magnetic field H_{c2} of layered dichalcogenide metals (no contribution of the paramagnetic effect to H_{c2} has been noted in $2H$-$NbSe_2$, [10] while in the intercalated compound $TaS_2(Py)_{1/2}$ the value of H_{c2} greatly exceeds H_p[11]). It is indicated also in the same section that measurement of the anisotropic Knight shift in the superconducting state makes it possible to distinguish between the mechanism proposed by us for the suppression of the contribution of the paramagnetic effect in H_{c2} and other mechanisms. In Sec. 4 we discuss also the possibility of experimentally observing the contribution of the spin-orbit interaction to the paramagnetic susceptibility and to the value of H_{c2} of weakly anisotropic superconductors with a lattice of the pyroelectric class.

We note that some of the results reported in this article were published earlier in compact form in[12] (effect of spin-orbit interaction on the value of χ of weakly anisotropic pyroelectric superconductors) and[13] (the value of H_{ps} in pure layered superconductors without symmetry center), and is reflected in the review of one of us[14] dealing with layered superconductors.

1. SPIN-ORBIT INTERACTION IN CRYSTALS OF THE PYROELECTRIC CLASS AND IN LAYERED CRYSTALS WITH INCOMMENSURATE CHARGE-DENSITY WAVE

In the absence of a magnetic field, the wave function of the ground state of the superconductor is constructed of paired single-electron states, which are mutually complex-conjugate. Such states in a system without a magnetic field are degenerate in energy (owing to the symmetry of the system with respect to time reversal), and are unstable below T_c relative to superconducting Cooper pairing. The spin-orbit interaction is of the form

$$V_{so} = \frac{\hbar}{4m^2c^2}[\nabla V(\mathbf{r}) \times \mathbf{p}]\sigma, \tag{1}$$

where m is the electron mass, c is the speed of light,

$V(\mathbf{r})$ is the periodic lattice potential, $\mathbf{p}$ is the electron-momentum operator, and σ is a Pauli operator.

The interaction (1) does not change the symmetry of the system relative to time reversal, so that in a crystal with any spatial symmetry it does not influence the thermodynamic characteristics of the superconducting phase. The spin-orbit interaction can in principle, however, change the paramagnetic properties of a superconductor, since this interaction itself (without the magnetic field) leads to a dependence of the energy of the single-electron state on the spin state of the electron. In fact, however, this dependence appears only in crystals without a symmetry center. Actually, if T is the Hermitian-conjugation operator and P is the space-inversion operator, then the states describable by Bloch functions

$$T\varphi_{\mathbf{k}}(\mathbf{r}) = Tu_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}}, \quad P\varphi_{\mathbf{k}}(\mathbf{r}) = Pu_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{kr}}$$

(here $u_{\mathbf{k}}(\mathbf{r})$ are spinors) have in crystals with symmetry centers identical quasimomenta $(-\mathbf{k})$ and identical energies, inasmuch as the spin-orbit interaction is invariant with respect to replacement of the time t by $-t$ and of the coordinate $\mathbf{r}$ by $-\mathbf{r}$. Thus, in a state with given quasimomentum there exists at least twofold degeneracy, and this degeneracy is connected with the spin variable of the electron.

In a crystal without a symmetry center, the single-electron energies depend on the spin, and the dependence of the electron energy operator $\hat{E}(\mathbf{k})$ with a given quasimomentum $\mathbf{k}$ on the spin operator σ, with allowance for the magnetic field $\mathbf{H}$, takes the form[15]

$$\hat{E}(\mathbf{k}) = E_0(\mathbf{k}) + \sigma\mathbf{h} + \sigma\mathbf{E}_1(\mathbf{k}), \tag{2}$$

where $\mathbf{h} = \frac{1}{2} g \mu_B \mathbf{H}$, $E_0(\mathbf{k})$ is the spin-independent part of the electron energy, and the pseudovector $\mathbf{E}_1(\mathbf{k})$ reverses sign when $\mathbf{k}$ is replaced by $-\mathbf{k}$ because of the invariance of the system to time reversal (replacement of σ by $-\sigma$ and of $\mathbf{k}$ by $-\mathbf{k}$). If the system has also a symmetry center, then the condition $\mathbf{E}_1(\mathbf{k}) = \mathbf{E}_1(-\mathbf{k})$ must also be satisfied, and in this case we have of necessity $\mathbf{E}_1(\mathbf{k}) \equiv 0$.

In first-order perturbation theory in the spin-orbit interaction we have

$$\mathbf{E}_1(\mathbf{k}) = \int \varphi_{\mathbf{k}}^*(\mathbf{r}) \frac{\hbar}{4m^2c^2} [\nabla V \times \mathbf{p}] \varphi_{\mathbf{k}}(\mathbf{r}) d^3\mathbf{r}, \tag{3}$$

where $\varphi_{\mathbf{k}}(\mathbf{r})$ is the spatial part of the Bloch function of the electron, obtained without allowance for V_{so}. We shall henceforth be interested in the expression for $\mathbf{E}_1(\mathbf{k})$ for momenta on the Fermi surface, and will consider therefore only the dependence of $\mathbf{E}_1$ on the vector $\mathbf{n}$, which determines the quasimomentum direction $(\mathbf{n} = \mathbf{k}/k_F)$.

In pyroelectric metals, the expression for $\mathbf{E}_1(\mathbf{n})$ can be written in the form

$$\mathbf{E}_1(\mathbf{n}) = [\boldsymbol{\varepsilon}_1 \times \mathbf{n}], \tag{4}$$

where $\boldsymbol{\varepsilon}_1$ is a vector directed along the polar axis. Expression (4) is in this case the first term of the expansion of $\mathbf{E}_1(\mathbf{n})$ in spherical functions.

In the investigation of layered crystals we shall neglect the motion of the electron in a direction perpendicular to the layers. This approximation is fully justified for intercalated crystals and crystals of the type $4Hb$-TaS_2 with alternating semiconducting and metallic layers, inasmuch as in these crystals the conductivity transverse to the layers is at least three orders of magnitude smaller than the conductivity along the layers and has a nonmetallic character.[14,16,17] In the layered metals $2H$-$NbSe_2$ and $2H$-TaS_2 the anisotropy of the conductivity does not exceed 50, and according to Schwall *et al.*[18] the anisotropy of the effective mass in $2H$-$NbSe_2$ is approximately equal to 16. For $2H$ modifications of layered metals, the neglect of the transverse motion of the electrons is less justified, but it can be assumed that the results obtained within the framework of this approximation are valid at least qualitatively.

As already noted above, the lattice of the high-temperature phase of a layered metal is hexagonal and has a symmetry center. But when the temperature is lowered, structural transitions with formation of a charge-density wave (CDW) within the layers is observed in all sufficiently pure layered non-intercalated metals. A CDW structural transition appears in layered metals because "nesting" sections or saddle points are present on the Fermi surface (which is practically two-dimensional).[6,19] Such singularities of the Fermi surface lead to a strong polarizability of the electrons under the influence of potential spatial harmonics with wave vectors that cause the "nesting" of the corresponding sections of the Fermi surface or the saddle points. Owing to the hexagonal symmetry, layered metals have three such wave vectors $(\mathbf{Q}_1, \mathbf{Q}_2, \mathbf{Q}_3)$, making angles 120° with one another.

Below the transition point, the strong polarizability of the electrons leads to the appearance of an ion-displacement wave inside the layer, with wave vectors $\mathbf{Q}_i$ $(i = 1, 2, 3)$, and an energy gap appears in this case on the "nesting" sections of the Fermi surface.

In addition to the lattice distortion, a charge-density wave is also produced, and the parameter of the CDW transition can be chosen to be the relative change of the electron density $\alpha(\mathbf{r})$, defined by the relation

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r})[1 + \alpha(\mathbf{r})], \tag{5}$$

where $\rho(\mathbf{r})$ is the electron density in the lattice with the CDW, and $\rho_0(\mathbf{r})$ is the electron density in the lattice without a superstructure.[20] Since we neglect the motion of the electrons between the layers, we shall henceforth be interested only in the superstructure inside the layer, and we shall consider only a two-dimensional lattice.

In a commensurate CDW, the displacement wave is tied to the initial lattice, and the symmetry center is preserved when the superstructure appears. In other words, the function $\alpha(\mathbf{r})$ turns out to be invariant to the replacement of $\mathbf{r}$ by $-\mathbf{r}$, if the origin is chosen to be the symmetry center of the initial lattice. Another situation

can be encountered only in the case of an incommensurate CDW. A realization of a superstructure $\alpha(\mathbf{r})$ without a symmetry center is not excluded in that case. This possibility is a result of the fact that in the lattice a superstructure with wave vectors $\mathbf{Q}_i$ must inevitably lead to the appearance of superstructures with wave vectors $m\mathbf{K}_i + n\mathbf{Q}_i$, where m and n are integers, while $\mathbf{K}_i$ are the reciprocal-lattice vectors of the main structure. If the superstructure $\mathbf{Q}_i$ is unique, then the free energy of the system reaches a minimum at its maximum symmetry, and the superstructure is centrally symmetrical (a complete lattice with incommensurate CDW may not have a symmetry center, but since the vectors $\mathbf{K}_i$ and $\mathbf{Q}_i$ are not commensurate, the contributions of the main structure and of the superstructure to any quantity are summed, and there are no interference terms). We shall show below that the appearance of superstructures $m\mathbf{K}_i + n\mathbf{Q}_i$ causes the centrally-symmetrical solution to be energywise unfavored, and the deviation from the CDW with symmetry center is larger the larger the amplitude of the superstructures $m\mathbf{K}_i + n\mathbf{Q}_i$. In layered metals, the vectors $\mathbf{Q}_i$ are very close to $\mathbf{K}_i/3$ (in $2H$-$NbSe_2$ their relative difference below T_c is approximately 0.01), and therefore the vectors $\mathbf{K}_i - 2\mathbf{Q}_i$ are also close to $\mathbf{K}_i/3$ and the amplitudes of the displacements with vectors $\mathbf{K}_i - 2\mathbf{Q}_i$ are comparable with the amplitude of the main superstructure $\mathbf{Q}_i$.[7] It is important also that the incommensurability of the CDW in $2H$-$NbSe_2$ is preserved at temperatures below T_c (down to 5 °K according to the data of[7] and to 1.3 °K according to the data of[21]). Thus, in the case $2H$-$NbSe_2$ one should expect an appreciable deviation of the superstructure from central symmetry.

Taking the foregoing considerations into account, we shall make allowance in $\alpha(\mathbf{r})$ only for the superstructures $\mathbf{Q}_i$ and $\mathbf{Q}_i' = \mathbf{K}_i - 2\mathbf{Q}_i$, and write down $\alpha(\mathbf{r})$, as well as the superlattice potential V_Q acting on the electrons, in the form

$$\alpha(\mathbf{r}) = \sum_i \psi_i(\mathbf{r}),$$

$$\psi_i(\mathbf{r}) = u_i \cos(\mathbf{Q}_i\mathbf{r} + \phi_i) + u_i' \cos(\mathbf{Q}_i'\mathbf{r} + \phi_i'),$$

$$V_Q(\mathbf{r}) = V_0(\mathbf{r}) \sum_i [v_i \cos(\mathbf{Q}_i\mathbf{r} + \phi_i) + v_i' \cos(\mathbf{Q}_i'\mathbf{r} + \phi_i')], \quad (6)$$

where ϕ_i and ϕ_i' are the phases of the superstructures and $V_0(\mathbf{r})$ is the potential of the initial lattice.

It is shown in the Appendix that the requirement that the free energy be a minimum determines the phases $\phi = \phi_1 + \phi_2 + \phi_3$ and $\gamma_i = 2\phi_i + \phi_i'$, and that in the general case the phases ϕ and γ_i differ from zero or π. Then the potential $V_Q(\mathbf{r})$ has no symmetry center (since the problem is two-dimensional, the origin can be so chosen that two of the three phases ϕ_i are equal to zero at π, so that the symmetry of the superlattice relative to inversion is determined by the quantities ϕ and γ_i).

In a lattice with potential (6), the vector $\mathbf{E}_1(\mathbf{k})$ defined by expression (3) differs from zero, and in the calculation of $\mathbf{E}_1(\mathbf{k})$ it is necessary to take into account the change of the Bloch functions of the electron under the influence of the superlattice potential V_Q. The potential V_Q is small in comparison with the potential of the main lattice $V_0(\mathbf{r})$. According to NMR quadrupole splitting data,[22] the change of the electric-field gradient in the charge-density wave of $2H$-$NbSe_2$ amounts to approximately 10%, and the change of the potential can be assumed to be approximately of the same order (i.e., $v_i, v_i' \approx 0.1$). Therefore, in principle, the vector $\mathbf{E}_1(\mathbf{k})$ can be calculated by perturbation theory in terms of the potential V_Q for all the vectors $\mathbf{k}$, except those that lie on the "nesting" sections of the Fermi surface or close to them (close to the saddle point in the saddle-point model). We shall not carry out these calculations, and indicate only the symmetry properties of the vector $\mathbf{E}_1(\mathbf{n})$, its dependence on the phase shifts ϕ and γ_i, and its order of magnitude.

In the model wherein the electrons execute two-dimensional motion, the vector $\mathbf{E}_1(\mathbf{n})$ is perpendicular to the layers, i.e., $\mathbf{E}_1(\mathbf{n}) = E_1(\mathbf{n})\mathbf{z}_0$, where $\mathbf{z}_0$ is a unit vector normal to the layers. Furthermore, $\mathbf{E}_1(\mathbf{n})$ depends only on the angle φ, which specifies the position of the vector $\mathbf{k}$ on the two-dimensional Fermi surface. Since $\mathbf{E}_1(\mathbf{n})$ is odd in $\mathbf{n}$, it follows that $E_1(\varphi) = -E_1(\pi + \varphi)$, and from the hexagonal symmetry of the lattice it follows that $E_1(\varphi) = E_1(\varphi + 2\pi/3)$. Confining ourselves to the first term of the expansion of $E_1(\varphi)$ in a Fourier series in φ, we obtain

$$E_1(\varphi) = \varepsilon_1 \sin(3\varphi + \varphi_0). \quad (7)$$

We now obtain the dependence of ε_1 on the phase shifts ϕ and γ_i. After integrating with respect to $\mathbf{r}$ in (3), a nonzero result is obtained only from those terms of the perturbation-series in V_Q which contain the products of the waves i with a summary wave vector equal to zero or to $\mathbf{K}_i$. In third-order perturbation theory there are two types of such terms, corresponding to the conditions $\mathbf{Q}_1 + \mathbf{Q}_2 + \mathbf{Q}_3 = 0$ and $2\mathbf{Q}_i + \mathbf{Q}_i' = \mathbf{K}_i$. They lead respectively to a dependence of ε_1 on the phase shifts ϕ and γ_i. Nonzero terms of higher orders in V_Q contain the same combinations of the wave vectors $\mathbf{Q}_i$ and $\mathbf{Q}_i'$, and also depend on ϕ and γ_i. It is shown in the Appendix that the minimum of the free energy is reached when all the γ_i are equal ($\gamma_i = \gamma$). Thus, ε_1 depends only on the phases ϕ and γ, and is furthermore an odd function of ϕ and γ. In the general case the phases ϕ and γ are not small and the deviation of the superstructure from central symmetry is comparable with the superstructure itself.

Let us estimate now the order of magnitude of ε_1. Since the contribution to ε_1 appears in third-order perturbation theory in V_Q, it follows that $\varepsilon_1 \sim \beta V_Q (V_Q/\Delta E)^2$, where β is a coefficient that takes into account the smallness of the potential with changing spin as compared with the usual potential $V_0(\mathbf{r})$ (in order of magnitude we have $\beta \sim (e^2 Z/\hbar c)^2$, where Z is the atomic number of the element), while ΔE is the average difference between the electron energies in the states $\mathbf{k}$ and $\mathbf{k} + \mathbf{Q}$. At $\beta \sim 10^{-1}$ and $V_Q^3/V_0(\Delta E)^2 \sim 10^{-2}$–$10^{-3}$ we obtain for ε_1 values from 1 to 50 °K.

We notice that the lattice with non-commensurate CDW is aperiodic, and the quasimomentum is not a real quantum number in this case. However, each state of

an electron in this lattice corresponds to a state with quasimomentum **k** in the main lattice without CDW. This is precisely the continuous quantity we use to characterize the electronic states in a lattice with incommensurate CDW.

In most investigated intercalated layered compounds, the CDW transition is suppressed.[6] It is completely absent, in particular, in the compound $TaS_2(Py)_{1/2}$. As already noted in the Introduction, the absence of a symmetry center in such crystals can be due to the distortion of the lattice under the influence of the molecules (at present there is no complete information on the lattice structure of intercalated compounds). The spin-orbit interaction in layered compounds with molecules can be described by expression (4) if the lattice of the layer had a preferred vector, or by expression (7) if there is no preferred vector but there is likewise no symmetry center. As we shall show below, in the approximation with two-dimensional motion of the electrons both expressions give the same result for the paramagnetic susceptibility of a superconductor and for the paramagnetic limit in the case of a field parallel to the layers.

2. PARAMETRIC SUSCEPTIBILITY OF A SUPERCONDUCTOR WITH A LATTICE WITHOUT SYMMETRY CENTER

Susceptibility of pure superconductors. Expressing the spin operator of the energy of an electron with quasimomentum **k** in the form (2), we can write down the Gor'kov equations for the Green's function $G(\mathbf{r},\mathbf{r}') \equiv G_{\alpha\beta}(\mathbf{r},\mathbf{r}')$, for the anomalous function $F(\mathbf{r},\mathbf{r}') \equiv F_{\alpha\beta}(\mathbf{r},\mathbf{r}')$, and for the order parameter $\Delta(\mathbf{r})$. We shall consider next only the homogeneous solutions for the order parameter. Then the equations for the Fourier components $\hat{G}(\mathbf{k})$ and $\hat{F}(\mathbf{k})$ are, in the frequency representation,

$$[i\omega-\hat{E}(\mathbf{k})]\hat{G}_\omega(\mathbf{k})-\Delta\hat{F}_\omega^+(\mathbf{k})=I, \quad [-i\omega-\hat{E}^+(-\mathbf{k})]\hat{F}_\omega^+(\mathbf{k})+\Delta\hat{G}_\omega(\mathbf{k})=0;$$
$$\hat{\Delta}=\Delta I=\lambda\sum_{\omega,\mathbf{k}}\hat{F}_\omega^+(\mathbf{k}), \quad \omega=2\pi T\left(n+\frac{1}{2}\right). \tag{8}$$

From (8) we obtain for the paramagnetic moment of the superconductor **M** in a weak field **H** the expression (in units of $g\mu_B/2$)

$$\mathbf{M}=-T\sum_\omega\int\frac{d\mathbf{k}}{2\pi}\,\mathrm{Sp}\,\boldsymbol{\sigma}[\hat{G}_\omega(\mathbf{k})(\boldsymbol{\sigma}\mathbf{h})\hat{G}_\omega(\mathbf{k})+\hat{F}_\omega(\mathbf{k})(\boldsymbol{\sigma}\mathbf{h})\hat{F}_\omega^+(\mathbf{k})], \tag{9}$$

in which the Green's functions are calculated at $\mathbf{H}=0$.

It follows from (8) that the dependence of the Green's functions on the spin matrices can be separated by taking them in the form

$$\hat{G}_\omega(\mathbf{k})=\frac{1}{2}\sum_s(1+s\boldsymbol{\sigma}\mathbf{e})G_{\omega s}(\mathbf{k}); \quad \mathbf{e}=\frac{\mathbf{E}_1(\mathbf{n})}{|\mathbf{E}_1(\mathbf{n})|}$$
$$\hat{F}_\omega(\mathbf{k})=\frac{1}{2}\sum_s(1+s\boldsymbol{\sigma}\mathbf{e})F_{\omega s}(\mathbf{k}); \quad s=\pm1, \quad \mathbf{n}=\frac{\mathbf{k}}{k_F}. \tag{10}$$

Multiplying from the left Eqs. (8) at $H=0$ by $1+s\boldsymbol{\sigma}\cdot\mathbf{e}$ we obtain for $G_{\omega s}(\mathbf{k})$ and $F_{\omega s}(\mathbf{k})$ the usual expressions

$$G_{\omega s}(\mathbf{k})=-\frac{i\omega+E_s(\mathbf{k})}{\omega^2+\Delta^2+E_s^2(\mathbf{k})}, \quad F_{\omega s}(\mathbf{k})=\frac{\Delta}{\omega^2+\Delta^2+E_s^2(\mathbf{k})}, \tag{11}$$
$$E_s(\mathbf{k})=E_0(\mathbf{k})+s|\mathbf{E}_1(\mathbf{n})|.$$

It follows from (9) and (10) that the expression for the paramagnetic moment **M** can be written in the form

$$\mathbf{M}=-T\sum_{\omega,s,s'}\int\frac{d\mathbf{k}}{2\pi}\left[\frac{1}{2}(1-ss')\mathbf{h}+\mathbf{e}(\mathbf{eh})\right][G_{\omega s}(\mathbf{k})G_{\omega s'}(\mathbf{k})+F_{\omega s}(\mathbf{k})F_{\omega s'}(\mathbf{k})]. \tag{12}$$

We introduce the quantities $\chi_\pm(\mathbf{n})$ with the aid of the relations

$$\chi_\pm(\mathbf{n})=\frac{1}{2}\chi_n\int dE_0(\mathbf{k})\sum_{\omega,s,s'}(1\pm ss')[G_{\omega s}(\mathbf{k})G_{\omega s'}(\mathbf{k})+F_{\omega s}(\mathbf{k})F_{\omega s'}(\mathbf{k})], \tag{13}$$

where χ_n is the paramagnetic susceptibility of the metal in the normal state. Then the expression for **M** can be represented in the form

$$\mathbf{M}=\frac{1}{4\pi}\int d\mathbf{n}\{\chi_-(\mathbf{n})\mathbf{h}+\mathbf{e}(\mathbf{n})(\mathbf{e}(\mathbf{n})\mathbf{h})[\chi_+(\mathbf{n})-\chi_-(\mathbf{n})]\}. \tag{14}$$

The quantity χ_+ does not depend on the spin-orbit interaction and is equal to the paramagnetic susceptibility χ_0 of an ordinary superconductor.

We integrate with respect to energy in the expression for $\chi_\pm(\mathbf{n})$, assuming the $E_0(\mathbf{k})$ spectrum to be isotropic and $\varepsilon_1 \ll \hbar\omega_D$ ($\mathbf{k}=(k_x,k_y,k_z)$ in a pyroelectric and $\mathbf{k}=(k_x,k_y)$ in a layered compound. Then

$$\chi_-(\mathbf{n})=\chi_n\left\{1-\pi T\Delta^2\sum_\omega\frac{1}{(\omega^2+\Delta^2)^{1/2}[\omega^2+\Delta^2+E_1^2(\mathbf{n})]}\right\}, \tag{15}$$
$$\chi_+(\mathbf{n})=\chi_0(T)=\chi_n\left[1-\pi T\Delta^2\sum_\omega\frac{1}{(\omega^2+\Delta^2)^{3/2}}\right].$$

For a pure layered superconductor we obtain after integrating with respect to the angles the following result for the susceptibilities $\chi_\parallel$ and $\chi_\perp$ along and across the layers:

$$\chi_\parallel(T)=\chi_n\left[1-\pi T\Delta^2\sum_\omega\frac{1}{(\omega^2+\Delta^2+\varepsilon^2)^{1/2}(\omega^2+\Delta^2)}\right] \tag{16}$$
$$\chi_\perp(T)=\chi_0(T).$$

As $T\to0$ we obtain

$$\chi_\parallel(0)=\chi_n\left[1-\frac{\Delta(0)}{\varepsilon_1}\operatorname{arctg}\frac{\varepsilon_1}{\Delta(0)}\right], \quad \chi_\perp(0)=0. \tag{17}$$

Let us determine the character of the angular dependence of the susceptibility for a pyroelectric superconductor in the case when the field **H** is directed at an arbitrary angle relative to the polar axis. Recognizing that the quantities $\chi_\pm(\mathbf{n})$ depend only on the angle θ between the direction of the field and the polar axis, we average in (14) over the angle in the plane perpendicular to this axis. It is easily seen that $\langle e_ie_j\rangle=\frac{1}{2}\delta_{ij}$ for $(i,j)=(x,y)$ and $\langle e_ie_j\rangle=0$ if $i=z$ or $j=z$ (the z axis is chosen to be the polar axis). Taking this into account, the expression (14) becomes

$$\mathbf{M}=\int\frac{d\mathbf{n}}{4\pi}\left\{\chi_-(\mathbf{n})\mathbf{a}(\mathbf{aH})+\frac{1}{2}[\chi_-(\mathbf{n})+\chi_+(\mathbf{n})][\mathbf{H}-\mathbf{a}(\mathbf{aH})]\right\}, \tag{18}$$

where **a** is a unit vector along the polar axis.

Thus, the susceptibility is a second-rank tensor. Integrating with respect to **n**, we obtain ultimately

$$\chi_{\parallel}=\chi_n\left\{1-\pi T\Delta^2\sum_{\omega}\frac{1}{\varepsilon_1\Omega(\Omega^2+\varepsilon_1^2)^{1/2}}\ln\frac{(\Omega^2+\varepsilon_1^2)^{1/2}+\varepsilon_1}{\Omega}\right\},$$
$$\chi_{\perp}=\tfrac{1}{2}\chi_0+\tfrac{1}{2}\chi_{\parallel},\quad \Omega=(\omega^2+\Delta^2)^{1/2}. \tag{19}$$

At $T=0$ we have

$$\chi_{\parallel}=\chi_n\left\{1-\frac{1}{\alpha}\int_0^{\pi/2}\frac{d\theta}{[1+(\alpha\sin\theta)^2]^{1/2}}\ln[(1+(\alpha\sin\theta)^2)^{1/2}+\alpha\sin\theta]\right\}, \tag{20}$$
$$\chi_{\perp}=\tfrac{1}{2}\chi_{\parallel},$$

where $\alpha=\varepsilon_1/\Delta$. At $\alpha\gg 1$ we obtain

$$\chi_{\parallel}\approx 1-(\ln\alpha/\alpha)^2,\quad \chi_{\perp}=\chi_{\parallel}/2.$$

If the measurements of the Knight shift are carried out on small particles with polar axes randomly oriented relative to the magnetic field, we obtain with the aid of (18) $\langle\chi\rangle=(2\chi_{\parallel}+\chi_0)/3$. At $\varepsilon_1\gg\Delta$ we have $\langle\chi\rangle\approx\frac{2}{3}\chi_n+\frac{1}{3}\chi_0$, i.e., at $T=0$ the mean value of the susceptibility is equal to two-thirds of its value in the normal state.[12]

Susceptibility of layered superconductor with nonmagnetic impurities. According to the known results,[9] in the expressions for the Green's functions (10) and (11) for a superconductor with impurities it is necessary to replace the frequencies ω and the gap Δ by the quantities $\tilde{\omega}=\eta\omega$ and $\Delta=\eta\Delta$, where $\eta=1+\nu/\Omega$, $\nu=1/2\tau$ and τ is the time of scattering of the electron by the impurities. In addition, scattering by impurities changes the vertex part of the interaction of the superconducting with the magnetic field. We write down the vertex part of the interaction $\hat{\mathcal{T}}$ and of the Green's functions in the Nambu matrix representation.

For the vertex part $\hat{\mathcal{T}}_0$ of zeroth order in the impurities and for the Green's function $\mathcal{G}$ of the electron we have in the Nambu representation

$$\hat{\mathcal{T}}_0=\sigma h\tau_3,\quad \hat{\mathcal{G}}=\frac{1}{2}\sum_{s}(1+s\sigma\mathbf{e})G_{\omega s}. \tag{21}$$

In the ladder approximation we obtain for $\hat{\mathcal{T}}$ the equation

$$\hat{\mathcal{T}}=\hat{\mathcal{T}}_0+\frac{\nu}{4}\sum_{\mathbf{k},s,s'}(1+s\sigma\mathbf{e})\mathcal{G}_{\omega s}(\mathbf{k})\hat{\mathcal{T}}\mathcal{G}_{\omega s}(\mathbf{k})(1+s'\sigma\mathbf{e}). \tag{22}$$

The magnetic moment is expressed in terms of the Green's function and the vertex part $\hat{\mathcal{T}}$ with the aid of the expressions

$$\mathbf{M}=-T\sum_{\mathbf{k},\omega}\mathrm{Sp}\,\sigma\hat{\Pi}_{11},\quad \hat{\Pi}=\hat{\mathcal{G}}\hat{\mathcal{T}}\hat{\mathcal{G}}. \tag{23}$$

Equations (21)–(23) are general. We shall obtain their solutions only for a layered superconductor. In a field perpendicular to the layers, the susceptibility $\chi_{\perp}$ does not depend on the impurities and is determined by the same expression (16) as for an ordinary superconductor. We now obtain the susceptibility $\chi_{\parallel}$ for a field parallel to the layers.

It is seen from (22) that in the case of isotropic scattering by the impurities $\hat{\mathcal{T}}$ depends only on the frequency ω and does not depend on the momentum. The preferred direction in the dependence of $\mathcal{T}$ on the spin matrices is therefore governed only by the magnetic field. The solution of (22) can then be sought in the form $\hat{\mathcal{T}}=\sigma\cdot\mathbf{h}_0\gamma$, where $\mathbf{h}_0$ is the vector of the magnetic-field direction, and γ depends only on ω and is determined from the equation

$$\gamma(\omega)=\gamma_0+\frac{\nu}{4}\sum_{\mathbf{k},s,s'}(1-ss')\mathcal{G}_{\omega s}(\mathbf{k})\gamma(\omega)\mathcal{G}_{\omega s'}(\mathbf{k}),\quad \gamma_0=h\tau_3\equiv h\begin{pmatrix}1&0\\0&-1\end{pmatrix}. \tag{24}$$

For $\chi_{\parallel}$ we obtain

$$\chi_{\parallel}=-\lim_{h\to 0}\frac{(g\mu_B)^2T}{4h}\sum_{\omega}\Pi_{11}(\omega),$$
$$\Pi(\omega)=\frac{1}{2}\sum_{\mathbf{k},s,s'}(1-ss')\mathcal{G}_{\omega s}(\mathbf{k})\gamma(\omega)\mathcal{G}_{\omega s'}(\mathbf{k}). \tag{25}$$

From (24) follows an equation for Π in the form

$$\Pi(\omega)=h\mathcal{P}_3(\omega)+\frac{1}{2}\nu\sum_{\mathbf{k},s,s'}(1-ss')\mathcal{G}_{\omega s}(\mathbf{k})\Pi(\omega)\mathcal{G}_{\omega s'}(\mathbf{k}),$$
$$\mathcal{P}_3(\omega)=\frac{1}{4}\sum_{\mathbf{k},s,s'}(1-ss')\mathcal{G}_{\omega s}(\mathbf{k})\tau_3\mathcal{G}_{\omega s'}(\mathbf{k}). \tag{26}$$

Summing over the momenta in the expression for $\mathcal{P}_3(\omega)$, we obtain

$$\mathcal{P}_3(\omega)=P_{32}(\omega)i\tau_2+P_{33}(\omega)\tau_3,\quad i\tau_2=\begin{pmatrix}0&1\\-1&0\end{pmatrix}. \tag{27}$$

The solutions for $\Pi(\omega)$ have the same matrix form as $\mathcal{P}_3(\omega)$, i.e.,

$$\Pi(\omega)=\Pi_2(\omega)i\tau_2+\Pi_3(\omega)\tau_3, \tag{28}$$

and for the quantities $\Pi_2(\omega)$ and $\Pi_3(\omega)$ we have the system of algebraic equations

$$\Pi_3(\omega)=P_{33}(\omega)[h+\nu\Pi_3(\omega)]+\nu\Pi_2(\omega)P_{23}(\omega),$$
$$\Pi_2(\omega)=-[h+\nu\Pi_3(\omega)]P_{32}(\omega)+\nu\Pi_2(\omega)P_{22}(\omega),$$
$$\mathcal{P}_2(\omega)=\frac{1}{4}\sum_{\mathbf{k},s,s'}(1-ss')\mathcal{G}_{\omega s}(\mathbf{k})i\tau_2\mathcal{G}_{\omega s'}(\mathbf{k})=P_{22}(\omega)i\tau_2+P_{23}(\omega)\tau_3. \tag{29}$$

The problem has been reduced to summation over the momenta in the expressions for P_{ik} with $i,k=2,3$. From summation over the momenta we go over in the usual manner to integration over the energy E_0 and the angle variable φ. Integration with respect to energy in the expressions for $\mathcal{P}_2$ and P_{32} can be carried out between infinite limits. The integration with respect to E_0 in the expression for P_{33} will be represented in the form of the difference between the integral J_1 from $-\infty$ to $+\infty$ and the integral J_2 from $-\infty$ to $-E_F$. When the second integral J_2 is substituted in the expression for $\chi_{\parallel}$ we obtain the susceptibility of the metal in the normal state. The quantities $\mathcal{P}_2$, P_{32}, and J_1 take the form

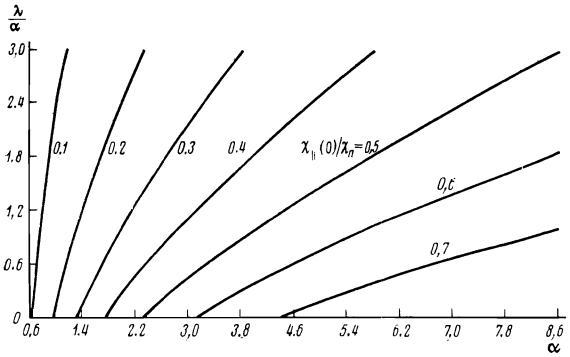

FIG. 1. Levels of constant values of the relative magnetic susceptibility $\chi_{\parallel}^{(0)}/\chi_n$ for layered superconductors as functions of the parameters $\lambda/\alpha = 1/2\tau\varepsilon_1$ and $\alpha = \varepsilon_1/\Delta(0)$.

$$P_{23}=\frac{2\pi\tilde{\omega}^2}{\tilde{\Omega}^2(\tilde{\Omega}^2+\varepsilon_1^2)^{1/2}},\quad P_{23}=-P_{32}=-\frac{\pi\tilde{\omega}\tilde{\Delta}}{\tilde{\Omega}^2(\tilde{\Omega}^2+\varepsilon_1^2)^{1/2}},$$
$$J_1=\frac{\pi\tilde{\Delta}^2}{\tilde{\Omega}^2(\tilde{\Omega}^2+\varepsilon_1^2)^{1/2}},\quad \tilde{\Omega}^2=\tilde{\omega}^2+\tilde{\Delta}^2. \tag{30}$$

We ultimately obtain

$$\frac{\chi_{\parallel}(T)}{\chi_n}=1-\pi T\Delta^2\sum_{\omega}\frac{1}{(\omega^2+\Delta^2)\{[((\omega^2+\Delta^2)^{1/2}+\nu)^2+\varepsilon_1^2]^{1/2}-\nu\}}. \tag{31}$$

As $T\to 0$ it follows from (31) that

$$\frac{\chi_{\parallel}(0)}{\chi_n}=1-\int_0^{\pi/2}\frac{dx}{[(\lambda+\sec x)^2+\alpha^2]^{1/2}-\lambda},\quad \lambda=\frac{\nu}{\Delta(0)},\quad \alpha=\frac{\varepsilon_1}{\Delta(0)}. \tag{32}$$

At $\lambda\gg\alpha$, accurate to terms $(\alpha/\lambda)^2$, we have

$$\chi_{\parallel}(0)/\chi_n=1-\pi a/2+2a^2F(a),\quad a=2\lambda/\alpha^2,$$
$$F(a)=\begin{cases}(a^2-1)^{-1/2}\operatorname{arctg}x(a), & x(a)=\left(\frac{a-1}{a+1}\right)^{1/2},\quad a>1\\ (1-a^2)^{-1/2}\ln\frac{1+x(a)}{1-x(a)}, & x(a)=\left(\frac{1-a}{1+a}\right)^{1/2},\quad a<1\end{cases} \tag{33}$$

It is seen from (33) that scattering by impurities suppresses the effect of the strong ($\alpha\to 1$) spin-orbit interaction only in the very dirty limit $\lambda\gg\alpha^2$ and

$$\chi_{\parallel}(0)/\chi_n=(\pi/4-1/2)\alpha^2/2\lambda,\quad \lambda\gg\alpha^2\gg\alpha,$$
$$\chi_{\parallel}(0)/\chi_n=1-\pi\lambda/\alpha^2,\quad \alpha^2\gg\lambda\gg\alpha. \tag{34}$$

The results of the numerical calculations for the paramagnetic susceptibility are shown in Fig. 1.

3. PARAMAGNETIC LIMIT FOR THE UPPER CRITICAL MAGNETIC FIELD OF A SUPERCONDUCTOR WITH A LATTICE WITHOUT IMPURITY CENTERS

In this section we calculate the upper critical magnetic field H_{c2} of a superconductor under the assumption that there is no orbital effect at all ($H_{c2}^*=\infty$) and that the transition from the normal state to the superconducting state is of second order. Then the upper critical field H_{ps}, which is determined by the paramagnetic effect, is determined from Eq. (8) subject to the condition $\Delta\to 0$. With allowance for the scattering by the impurities, we obtain the equation

$$1=\frac{\lambda}{2}\operatorname{Sp}\sum_{\omega,\mathbf{k}}\langle\hat{G}_{-\omega}(-\mathbf{k})\sigma_y\hat{G}_{\omega}^{+}(\mathbf{k})\sigma_y\rangle, \tag{35}$$

where $\langle\cdots\rangle$ denotes averaging of the product of the two-electron Green's function over the impurities. We introduce the Green's function of two electrons moving in a doped crystal

$$\langle\hat{K}_{\omega}(\mathbf{r},\mathbf{r}')\rangle=\langle\hat{G}_{-\omega}(\mathbf{r},\mathbf{r}')\otimes\hat{G}_{\omega}(\mathbf{r},\mathbf{r}')\rangle, \tag{36}$$

where $\otimes$ in the right-hand side denotes the direct product of the matrices $\hat{G}_{-\omega}(\mathbf{r},\mathbf{r}')$ and $\hat{G}_{\omega}(\mathbf{r},\mathbf{r}')$.

In the ladder approximation we obtain an equation for $\langle\hat{K}_{\omega}(\mathbf{r},\mathbf{r}')\rangle$:

$$\langle\hat{K}_{\omega}(\mathbf{r},\mathbf{r}')\rangle=\hat{K}_{\omega}(\mathbf{r},\mathbf{r}')+\frac{\nu}{2\pi N(0)}\int d\mathbf{r}_1\,\hat{K}_{\omega}(\mathbf{r},\mathbf{r}_1)\langle\hat{K}_{\omega}(\mathbf{r}_1,\mathbf{r}')\rangle,$$
$$\hat{K}_{\omega}(\mathbf{r},\mathbf{r}')=\langle\hat{G}_{-\omega}(\mathbf{r},\mathbf{r}')\rangle\otimes\langle\hat{G}_{\omega}(\mathbf{r},\mathbf{r}')\rangle, \tag{37}$$

and the Green's function $\langle\hat{G}_{\omega}(\mathbf{r},\mathbf{r}')\rangle$, which takes into account the scattering of the electron by the impurities, is obtained from the Green's functions of the ideal metal by replacing ω by $\tilde{\omega}=\omega+\nu\,\operatorname{sign}\omega$. Equations (35)–(37) are transformed into

$$1=\frac{1}{2}\lambda\sum_{\omega,\alpha\beta\gamma\delta}\Pi_{\alpha\beta,\gamma\delta}(\omega)(\sigma_y)_{\beta\gamma}(\sigma_y)_{\delta\alpha},\qquad \hat{K}_{\omega}(\mathbf{k})=\langle\hat{G}_{-\omega}(-\mathbf{k})\rangle\otimes\langle\hat{G}_{\omega}(\mathbf{k})\rangle,$$
$$\hat{\Pi}(\omega)=\sum_{\mathbf{k}}\left[\hat{K}_{\omega}(\mathbf{k})+\frac{\nu}{2\pi N(0)}\hat{K}_{\omega}(\mathbf{k})\hat{\Pi}(\omega)\right]. \tag{38}$$

Introducing the matrix

$$\hat{S}(\omega)\equiv S_{\alpha\beta}(\omega)=\sum_{\alpha',\gamma,\delta}\Pi_{\alpha\alpha',\gamma\delta}(\sigma_y)_{\alpha'\gamma}(\sigma_y)_{\delta\beta}, \tag{39}$$

we obtain from (38)

$$1=\frac{1}{2}\operatorname{Sp}\sum_{\omega}\hat{S}(\omega),$$
$$\hat{S}(\omega)=\sum_{\mathbf{k}}\left[\hat{S}_0(\omega,\mathbf{k})+\frac{\nu}{2\pi N(0)}\langle\hat{G}_{-\omega}(\mathbf{k})\rangle\hat{S}(\omega)\langle\hat{G}_{\omega}^{+}(\mathbf{k})\rangle\right], \tag{40}$$
$$\hat{S}_0(\omega,\mathbf{k})=\langle\hat{G}_{-\omega}(-\mathbf{k})\rangle\langle\hat{G}_{\omega}^{+}(\mathbf{k})\rangle,$$

where G^+ is the Hermitian adjoint of G and is obtained from G by replacing the operator $\hat{\sigma}$ by $-\hat{\sigma}$. For a field perpendicular to the vector $\mathbf{E}_1(\mathbf{n})$ we obtain after solving the matrix equation and summing over the momenta the following expression, from which we determine the dependence of H_{ps} on T:

$$\ln\frac{T_c}{T}=2\pi T\sum_{\omega>0}\frac{\tilde{\omega}h^2}{\omega[\omega(B-\nu\tilde{\omega})+\nu h^2]},$$
$$B^{-1}=\frac{1}{4\pi}\int\frac{d\mathbf{n}}{\tilde{\omega}^2+h^2+E_1^2(\mathbf{n})}. \tag{41}$$

For layered superconductors, the condition $\mathbf{H}\perp\mathbf{E}_1(\mathbf{k})$ is realized in the case of fields parallel to the layers. Then

$$B=[(\tilde{\omega}^2+h^2)(\tilde{\omega}^2+h^2+\varepsilon_1^2)]^{1/2}, \tag{42}$$

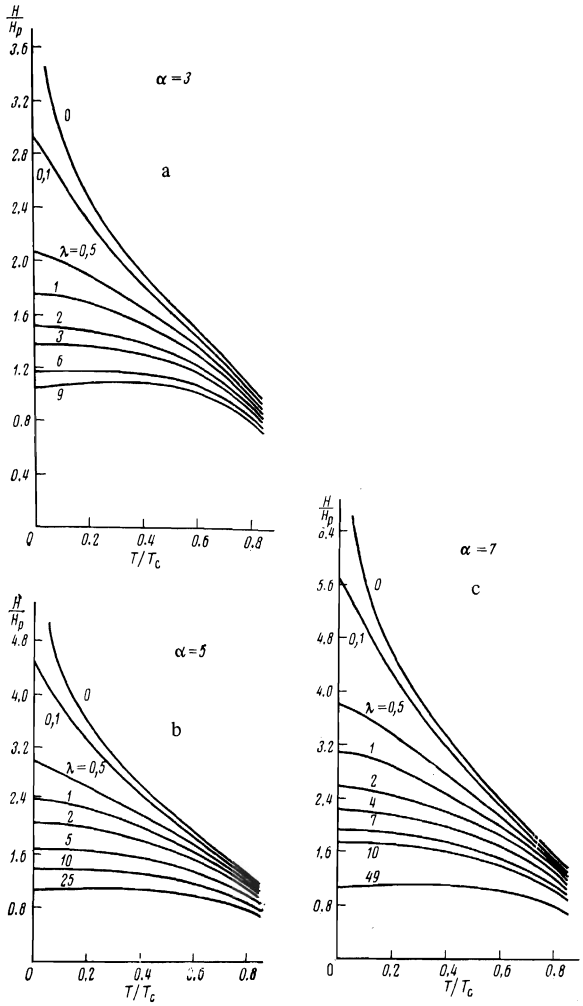

FIG. 2. Dependence of the excess above the paramagnetic limit H_{ps}/H_p on the temperature and on the degree of purity of the crystal $\lambda = 1/2\tau\Delta(0)$ at different values of the spin-orbit interaction parameter $\alpha = \varepsilon_1/\Delta(0)$: a) $\alpha = 3$, b) $\alpha = 5$, c) $\alpha = 7$.

and at $\nu = 0$ we have the previously obtained equation[13].

For a pyroelectric superconductor in a field parallel to the polar axis we have

$$B = \varepsilon_1(\tilde{\omega}^2 + h^2 + \varepsilon_1^2)^{1/2}/\ln\left[\left(1 + \frac{\varepsilon_1^2}{\tilde{\omega}^2 + h^2}\right)^{1/2} + \frac{\varepsilon_1}{(\tilde{\omega}^2 + h^2)^{1/2}}\right]. \quad (43)$$

At $\nu = 0$ and as $\omega \to 0$ we have $h^2 B^{-1} < 1$, so that for pure superconductors $h_{ps} \to \infty$ as $T \to 0$ when the field is parallel to the layers in layered compounds or is parallel to the polar vector ε_1 in pyroelectrics. The field h_{ps} remains finite in the presence of impurities, and also at $T > 0$.

At $\nu \gg \varepsilon_1$, accurate to terms $(\varepsilon_1/\nu)^2$, we have

$$\ln\frac{T_c}{T} = 2\pi T \sum_{\omega>0} \frac{h^2}{\omega[\omega^2 + h^2 + C\varepsilon_1^2\omega/\tilde{\omega}]}, \quad (44)$$

where $C = \frac{1}{2}$ for layered systems and $\frac{2}{3}$ for pyroelectrics. It is seen from (44) that, just as for the paramagnetic susceptibility, the scattering by the impurities suppresses the effect of the spin-orbit interaction on the paramagnetic limit at $\lambda \gg \alpha^2$.

Near T_c at $\lambda \ll \alpha^2$ and $\alpha \gg 1$ we obtain from (41) and (42) for $h_{ps\parallel}(T)$ of layered superconductors:

$$h_{ps\parallel}^2(T) = \frac{4}{\pi}(T_c - T)[(\varepsilon_1^2 + \nu^2)^{1/2} - \nu]. \quad (45)$$

Figures 2a, 2b, and 2c show the temperature dependence of H_{ps}/H_p at various values of the parameters α and λ. At $\lambda \approx \alpha^2$, the slope of the plot of H_{c2} against T becomes positive at $T < 0.55T_c$, thus indicating that the transition from the superconducting to the normal state is in fact of first order. At $\lambda < \alpha^2$ the critical field increases with decreasing temperature, i.e., a second order phase transition destroys the superconducting state if the spin-orbit interaction is strong enough. Figure 3 shows the dependence of H_{ps} on the parameters λ and α at $T = 0$.

4. DISCUSSION OF THE RESULTS AND OF THE EXPERIMENTAL DATA

Let us compare the effect of the spin-orbit interaction on the paramagnetic properties of a superconductor having a lattice without symmetry center with the effect of the spin-orbit scattering of electrons by impurities. In the first case the characteristic energy of the effect is $\varepsilon_1 \sim \beta V_0 \rho$, where ρ is a small parameter that takes into account the degree of deviation of the lattice from central symmetry (the parameter in a lattice with incommensurate CDW is $\rho \sim V_Q^3/V_0(\Delta E)^2$). In spin-orbit scattering, the characteristic energy is $\hbar/\tau_{so} \sim \beta^2\hbar\nu \sim n\beta^2 \cdot V_0^2/E_F$, where τ_{so} is the spin-orbit scattering time and n is the impurity concentration. For compounds with lattice without inversion center and with small impurity concentration, or for compounds of light elements (small β), the spin-orbit interaction is apparently the only mechanism capable of substantially influencing the paramagnetic properties of the superconductor. We note that the two discussed mechanisms that alter the paramagnetic properties can be distinguished from each other experimentally—only the spin-orbit interaction can lead to anisotropy of the paramagnetic properties and, in particular, to anisotropy of the Knight shift. To our knowledge, no measurements of the Knight shift in layered superconductors and in superconductors with lattice of the polar type have been made so far.

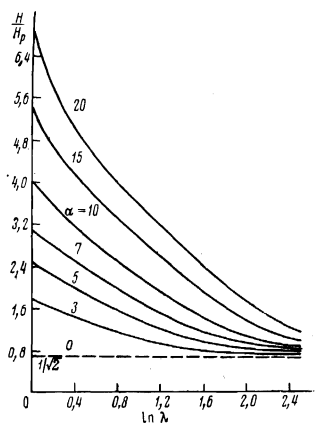

FIG. 3. Dependence of the excess of the paramagnetic limit H_{ps}/H_p at $T = 0$ as a function of the crystal-purity parameter $\lambda = 1/2\tau\Delta(0)$ for different values of the spin-orbit interaction parameter $\alpha = \varepsilon_1/\Delta(0)$.

We discuss now the possibilities of experimentally observing the changes of the paramagnetic limit in superconductors without impurity centers. Such changes can be observed only if the orbital upper critical field H_{c2}^* is strong enough in comparison with H_p ($H_{c2}^* \gtrsim H_p$). In bulky weakly anisotropic superconductors H_{c2}^* can be increased only by increasing the concentration of the nonmagnetic impurities. But scattering by impurities suppresses the effect of the spin-orbit interaction, and the paramagnetic Chandrasekhar–Clogston limit H_p can be appreciably exceeded only if $\varepsilon_1^2 \gg \nu T_c$. Therefore in weakly anisotropic superconductors the condition $H_{c2}^* \gtrsim H_{ps} > H_p$ can be satisfied under the rather stringent requirements $\varepsilon_1^2/T_c \gg \nu > mv_F$, where m is the mass of the free electron. These conditions can be satisfied in essence only in superconductors with sufficiently strong spin-orbit interaction. However, the condition $H_{c2}^* > H_p$ can be easily attained in films or small particles, so that measurements of the anisotropy of the Knight shift and of the upper critical field in such pyroelectric-superconductor samples would be of great interest. The paramagnetic limit H_{ps} is in this case maximal in a field parallel to the polar axis, and the quantity H_{ps} for this field direction is determined by Eqs. (41) and (43).

In strongly anisotropic systems, at definite directions of the magnetic field, the condition $H_{c2}^* \gtrsim H_p$ can be easily satisfied on account of the anisotropy of the motion of the electron even in the case of not very dirty crystals. In the effective-mass anisotropy in $2H$-$NbSe_2$ is of the order of 16, and for a field parallel to the layer, as $T \to 0$, the value of $H_{c2\parallel}^*$ determined from the data obtained for $-\partial H_{c2\parallel}/\partial T$ at $T \to T_c$ is approximately 120 kOe, while $H_p = 130$ kOe ($T_c = 7$ °K).[10] At 1.5 °K, experimental yields $H_{c2\parallel} = 130$ kOe and no lowering $H_{c2\parallel}$ on account of the paramagnetic effect is observed (the ordinary paramagnetic effect would yield for $2H$-$NbSe_2$ at $T = 0$ a value of $H_{c2\parallel}$ smaller by a factor 1.5–2 than $H_{c2\parallel}^*$). In $2H$-$NbSe_2$, as noted in Sec. 1 above, an incommensurate CDW structure is observed, and according to the estimates of Schwall *et al.*[18] we have $\lambda \approx 1$. It is therefore not excluded, in principle, that the suppression of the influence of the paramagnetic effect on $H_{c2\parallel}$ in this compound is due to the spin-orbit interaction of the electrons under conditions when there is no symmetry center.

The anisotropy of electrons motion in intercalated layered compounds is even larger than in $2H$-$NbSe_2$, and under the condition of very weak Josephson interaction of the layers, at temperatures not very close to T_c, the value of $H_{c2\parallel}^*$ is practically unlimited.[23–25] Under this situation, the field $H_{c2\parallel}$ is determined only by the paramagnetic effect. According to estimates made by one of us[14] and the experimental data of[18], the interaction of the layers in intercalated $TaS_2(Py)_{1/2}$ crystals at $H_{c2\parallel}(T)$ and $H_{c2\perp}(T)$ close to T_c is close to the Josephson interaction, and at low temperatures $H_{c2\parallel}^*$ can be regarded as infinite for this compound. At 1.4 °K, experiment yields $H_{c2\parallel} \geqslant 200$ kOe and $H_p = 60$ kOe ($T_c \approx 3.2$ K).[11] As already noted in Sec. 1, there are grounds for assuming that the $TaS_2(Py)_{1/2}$ lattice has no symmetry center, and so large an excess above the paramagnetic limit in this compound can therefore be attributed to spin-orbit interaction of the electrons with the lattice.[13]

It appears that another possible mechanism of suppressing the paramagnetic effect may be spin-orbit interaction of the electrons with impurities only.[24,26]1) Klemm *et al.*[24] emphasized that to explain the experimental data on $TaS_2(Py)_{1/2}$ it is necessary to have $\tau_{so} \lesssim 5 \cdot 10^{-14}$ sec (at $H_{c2}^* = \infty$ we have $H_{c2} = 0.602(\tau_{so}T_c)^{-1/2}H_p$). If we assume $\tau_{so} = 10\tau$ ($\beta \approx 0.3$), then the value of τ turns out to be very small, but still acceptable (optical investigation[27] yield for compounds with $TaS_{1.6}Se_{0.4}$ an electron optical scattering time $\tau \approx 4 \cdot 10^{-15}$ sec). The question of the causes of the suppression of the paramagnetic effect in $2H$-$NbSe_2$ and in $TaS_2(Py)_{1/2}$ still remains open. To answer it, the anisotropy of the Knight shift of these compounds must be measured.

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APPENDIX

We write down that part of the free energy $F(\alpha)$ which determines the phase shifts ϕ_i and ϕ_i' of the waves. Accurate to terms of fourth order in α, the free Landau energy is of the form[7,20]

$$F = F_1 + F_2;$$
$$F_1 = \int d\mathbf{r}\,[a(\mathbf{r})\alpha^2 + b(\mathbf{r})\alpha^3 + c(\mathbf{r})\alpha^4 - d(\mathbf{r})\,(|\psi_1\psi_2|^2 + |\psi_2\psi_3|^2 + |\psi_3\psi_1|^2)\,],$$
$$b(\mathbf{r}) = b_0 + b_1 \sum_i \cos \mathbf{K}_i\mathbf{r}, \qquad \text{(A.1)}$$

where F_2 contains gradient terms of no importance to us, and a, c, and d have the same coordinate dependence as b. From (A.1) we obtain for the free-energy terms that depend on the phase shifts ϕ_i and ϕ_i':

$$F(\phi_i\phi_i') = F_0 - \frac{3}{2} b_0 u_1 u_2 u_3 \cos\phi - \frac{1}{4} b_1 \sum_i u_i^2 v_i \cos\gamma_i + \frac{1}{4} c_1 u_1 u_2 u_3 \sum \cos(-\phi + \gamma_i). \qquad \text{(A.2)}$$

The minimum of F is reached at $u_i = u$ and $v_i = v$. It follows also from (A.2) that the minimum of F is reached at $\gamma_i = \gamma$. The phase shifts ϕ and γ are determined from the equations

$$A\sin\phi + B\sin(-\phi+\gamma) = 0, \quad A = {}^3/_2 b_0 u^3, \quad B = {}^3/_4 c_1 u^3 v,$$
$$D\sin\gamma - B\sin(-\phi+\gamma) = 0, \quad D = {}^3/_4 b_1 u^2 v. \qquad \text{(A.3)}$$

Equations (9) have a trivial solution $\sin\phi = \sin\gamma = 0$, which corresponds to the free energy

$$F = F_0 - A(-1)^m - B(-1)^n + D(-1)^{m+n}, \qquad \text{(A.4)}$$

where m and n are integers. In addition, at $|B/A + A/B - AB/D^2| \leqslant 2$ and $|B/D + D/B - DB/A^2| \leqslant 2$ we have the solutions

$$\cos\gamma = \frac{1}{2}\left(\frac{B}{A} + \frac{A}{B} - \frac{AB}{D^2}\right), \quad \cos\phi = \frac{1}{2}\left(\frac{B}{D} + \frac{D}{B} - \frac{DB}{A^2}\right) \qquad \text{(A.5)}$$

with energy

$$F=F_0-A-\frac{A}{2}\left[\frac{(D-B)^2}{BD}+\frac{BD}{A^2}\right]=F_0-D-\frac{D}{2}\left[\frac{(A-B)^2}{AB}+\frac{AB}{D^2}\right]. \quad (A.6)$$

From a comparison of (A.6) with (A.4) we see that if (ABD) is positive then a region of values of A, B, and D exists in which the energy of the nontrivial solution is smaller.

[1]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **42**, 1088 (1962) [Sov. Phys. JETP **15**, 752 (1962)].
[2]N. R. Werthamer, E. Helfand, and P. C. Hohenberg, Phys. Rev. **147**, 295 (1966).
[3]P. W. Anderson and E. J. Blount, Phys. Rev. Lett. **14**, 9 (1965).
[4]A. C. Lawson and W. H. Zachariasen, Phys. Lett. **38A**, 1 (1972).
[5]Yu. A. Izyumov, V. E. Naĭsh, and V. N. Syromyatnikov, Kristallografiya **21**, 256 (1976) [Sov. Phys. Crystallogr. 137 (1976)].
[6]J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).
[7]D. E. Moncton, J. D. Axe, and F. J. Di Salvo, Phys. Rev. Lett. **34**, 734 (1975).
[8]G. S. Parry, C. B. Scruby, and P. M. Williams, Philos. Mag. **29**, 601 (1974).
[9]A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Quantum Field Theoretical Methods in Statistical Physics), Fizmatgiz, 1962 [Pergamon, 1965].
[10]S. Foner and E. J. McNiff, Phys. Lett. **45A**, 429 (1973).
[11]R. C. Morris and R. V. Coleman, Phys. Rev. B **7**, 991 (1973).
[12]A. I. Rusinov, Kratk. Soobshch. Fiz. Akad. Nauk SSSR **9**, 19 (1972).
[13]L. N. Bulaevskiĭ and A. I. Rusinov, Pis'ma Zh. Eksp. Teor. Fiz. **21**, 147 (1975) [JETP Lett. **21**, 66 (1975)].
[14]L. N. Bulaevskiĭ, Usp. Fiz. Nauk **116**, 449 (1975) [Sov. Phys. Usp. **18**, 514 (1975)].
[15]C. Kittel, Quantum Theory of Solids, Wiley, 1963.
[16]A. H. Thompson, F. R. Gamble, and R. F. Koehler, Phys. Rev. B**5**, 2811 (1972).
[17]W. J. Wattamanjuk, J. P. Tidman, and R. F. Frindt, Phys. Rev. Lett. **35**, 62 (1975).
[18]R. E. Schwall, G. R. Stewart, and T. H. Geballe, J. Low Temp. Phys. **22**, 557 (1976).
[19]T. M. Rice and G. K. Scott, Phys. Rev. Lett. **35**, 120 (1975).
[20]W. L. McMillan, Phys. Rev. **B12**, 1187 (1975).
[21]M. Barmatz, L. R. Testardi, and F. J. Di Salvo, *ibid.*, 4367.
[22]E. Ehrenfreund, A. C. Gossard, F. R. Gamble, and T. H. Geball, J. Appl. Phys. **42**, 1491 (1971).
[23]L. N. Bulaevskiĭ and A. A. Guseinov, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 742 (1974) [JETP Lett. **19**, 382 (1974)].
[24]R. A. Klemm, A. Luther, and M. R. Beasley, Phys. Rev. B**12**, 877 (1975).
[25]N. Boccara, J P. Carton, and G. Sarma, Phys. Lett. **A49**, 165 (1974).
[26]L. N. Bulaevskiĭ, Zh. Eksp. Teor. Fiz. **64**, 2241 (1973); **65**, 1278 (1973) [Sov. Phys. JETP **37**, 1133 (1973); **38**, 634 (1974)].
[27]J. A. Benda, R. E. Howard, and W. A. Phillips, J. Phys. Chem. Solids **35**, 937 (1974).
[28]K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. **69**, 764 (1975) [Sov. Phys. JETP **42**, 390 (1976)].

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