Superconductivity in crystals without symmetry centers

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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 Y_Hf and V_Ru. 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 \( H_p \) of the upper critical magnetic field are obtained for such superconductors as functions of the relative spin-orbit interaction \( \alpha = \epsilon / \Delta(0) \), of the degree of purity of the crystals \( \lambda = 1/2 \Delta(0) \), of the temperature, and of the field direction. The quantities \( \chi \) and \( H_p \) are anisotropic, and \( H_p \) can greatly exceed the Chandrasekhar-Clogston paramagnetic limit \( H_p \). The experimental data for \( H_\alpha \) 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 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 \( H_{c2} \) of layered dichalcogenide metals (no contribution of the paramagnetic effect to \( H_{c2} \) has been noted in 2H-NbSe_2 \(^{10}\)) while the intercalated compound TaS_2(Py)_1/2 the value of \( H_{c2} \) greatly exceeds \( H_p \)). 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 \(^{11}\) (effect of spin–orbit interaction on the value of \( \chi \) of weakly anisotropic pyroelectric superconductors) and \(^{12}\) (the value of \( H_{c2} \) 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

\[
V_{so} = \frac{N}{4m^2c^2} [V(r) \times \sigma] \sigma,
\]

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 \( \sigma \) 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 electron energy on 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

\[
T \phi_k(\mathbf{r}) = T \phi_k(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}}, \quad P \phi_k(\mathbf{r}) = P \phi_k(\mathbf{r}) e^{-i \mathbf{k} \cdot \mathbf{r}}
\]

(here \( \phi_k(\mathbf{r}) \) are spinors) have in crystals with symmetry centers identical quasimomenta \( (\mathbf{k} - \mathbf{r}) \) 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 \( \sigma \), with allowance for the magnetic field \( \mathbf{H} \), takes the form

\[
E(k) = E(k) + \hbar \mathbf{\omega}(k) \mathbf{H} + \mathbf{\omega}(k) \mathbf{H} \mathbf{\omega}(k)
\]

where \( \hbar = \frac{1}{2} g \mu_B H \), \( E_0(k) \) is the spin-independent part of the electron energy, and the pseudovector \( \mathbf{E}_0(k) \) reverses sign when \( k \) is replaced by \( -k \) because of the invariance of the system to time reversal (replacement of \( \sigma \) by \( -\sigma \)) and of \( k \) by \( -k \). If the system has also a symmetry center, then the condition \( E_0(k) = E_0(-k) \) must also be satisfied, and in this case we have of necessity \( E_0(k) = 0 \).

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

\[
E_i(k) = \int \phi_i^*(\mathbf{r}) \frac{\hbar}{2m_e c} \mathbf{V} \cdot \mathbf{p} \phi_i(\mathbf{r}) \mathbf{e}^{i \mathbf{k} \cdot \mathbf{r}} d\mathbf{r},
\]

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

In pyroelectric metals, the expression for \( E_i(n) \) can be written in the form

\[
E_i(n) = [c_1 \times n],
\]

where \( c_1 \) is a vector directed along the polar axis. Ex-
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 this 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 $n\mathbf{K}_i + m\mathbf{Q}_i$, 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 $n\mathbf{K}_i + m\mathbf{Q}_i$ 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 $n\mathbf{K}_i + m\mathbf{Q}_i$. 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]

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 $V_\Omega$ acting on the electrons, in the form

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

$$\psi_i(\mathbf{r}) = u_i \cos (Q_i x + \phi_i) + u_i' \cos (Q_i y + \phi_i'),$$

$$V_\Omega(\mathbf{r}) = V_\Omega(\mathbf{r}) \sum [v_i \cos (Q_i x + \gamma_i) + v_i' \cos (Q_i y + \gamma_i')],$$

where $\phi_i$ and $\phi_i'$ are the phases of the superstructures and $V_\Omega(\mathbf{r})$ 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 $\gamma = 2\phi_1 + \phi_3$, and that in the general case the phases $\phi$ and $\gamma$ differ from zero or $\pi$. Then the potential $V_\Omega(\mathbf{r})$ has no symmetry center (since the problem is two-dimensional, the origin can be chosen so that two of the three phases $\phi_i$ are equal to zero at $\pi$, so that the symmetry of the superlattice relative to inversion is determined by the quantities $\phi$ and $\gamma_i$).

In a lattice with potential (6), the vector $E_\Omega(\mathbf{k})$ defined by expression (3) differs from zero, and in the calculation of $E_\Omega(\mathbf{k})$ it is necessary to take into account the change of the Bloch functions of the electron under the influence of the superlattice potential $V_\Omega$. The potential $V_\Omega$ is small in comparison with the potential of the main lattice $V_\Omega(\mathbf{r})$. According to NMR quadrupole splitting data, [281] the change of the electric-field gradient in the charge-density wave of $2H$-NbSe$_2$ amounts to approximately 10%_0, and the change of the potential can be assumed to be approximately of the same order (i.e., $\nu_0 V_\Omega = 0.1$). Therefore, in principle, the vector $E_\Omega(\mathbf{k})$ can be calculated by perturbation theory in terms of the potential $V_\Omega$ 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 $E_\Omega(\mathbf{n})$, its dependence on the phase shifts $\phi$ and $\gamma$, and its order of magnitude.

In the model wherein the electrons execute two-dimensional motion, the vector $E_\Omega(\mathbf{n})$ is perpendicular to the layers, i.e., $E_\Omega(\mathbf{n}) = E_\Omega(\mathbf{k}) z_0$, where $z_0$ is a unit vector normal to the layers. Furthermore, $E_\Omega(\mathbf{n})$ depends only on the angle $\varphi$, which specifies the position of the vector $\mathbf{k}$ on the two-dimensional Fermi surface. Since $E_\Omega(\mathbf{n})$ is odd in $n$, it follows that $E_\Omega(\varphi) = -E_\Omega(\pi + \varphi)$, and from the hexagonal symmetry of the lattice it follows that $E_\Omega(\varphi) = E_\Omega(\varphi + 2\pi/3)$. Confining ourselves to the first term of the expansion of $E_\Omega(\varphi)$ in a Fourier series in $\varphi$, we obtain

$$E_\Omega(\varphi) = 125 \sin (3\varphi + \psi).$$

We now obtain the dependence of $\epsilon_1$ on the phase shifts $\phi$ and $\gamma$. After integrating with respect to $\varphi$ in (3), a nonzero result is obtained only from those terms of the perturbation-series in $V_\Omega$ 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 $Q_1 + Q_2 + Q_3 = 0$ and $2Q_i + Q_i' = K_i$. They lead respectively to a dependence of $\epsilon_1$ on the phase shifts $\phi$ and $\gamma$. Nonzero terms of higher orders in $V_\Omega$ contain the same combinations of the wave vectors $\mathbf{Q}_i$ and $\mathbf{Q}_i'$, and also depend on $\phi$ and $\gamma$. It is shown in the Appendix that the minimum of the free energy is reached when all the $\gamma_i$ are equal ($\gamma = \gamma_i$). Thus, $\epsilon_1$ depends only on the phases $\phi$ and $\gamma$, and furthermore an odd function of $\phi$ and $\gamma$. In the general case the phases $\phi$ and $\gamma$ 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 $\epsilon_1$. Since the contribution to $\epsilon_1$ appears in third-order perturbation theory in $V_\Omega$, it follows that $\epsilon_1 \approx \beta V_\Omega(\Delta E)^2$, where $\beta$ is a coefficient that takes into account the smallness of the potential with changing spin as compared with the usual potential $V_\Omega(\mathbf{k})$ (in order of magnitude we have $\beta = (e^2 Z / \hbar c)^2$, where $Z$ is the atomic number of the element), while $\Delta E$ is the average difference between the electron energies in the states $\mathbf{k}$ and $\mathbf{k} + \mathbf{Q}$. At $\beta \approx 10^{-4}$ and $V_\Omega^2(\Delta E)^2 \approx 10^{-9}$ we obtain for $\epsilon_1$ 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 $\mathbf{k}$ 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. It is completely absent, in particular, in the compound TaS$_2$(Py)$_x$. 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 $\mathbf{k}$ in the form (2), we can write down the Gor'kov equations for the Green’s function $G_{\sigma} \left( \mathbf{r}, \mathbf{r}' \right)$, for the anomalous function $F_{\sigma} \left( \mathbf{r}, \mathbf{r}' \right)$, and for the order parameter $\Delta \left( \mathbf{r} \right)$. We shall consider next only the homogeneous solutions for the order parameter. Then the equations for the Fourier components $\tilde{G} \left( \mathbf{k} \right)$ and $\tilde{F} \left( \mathbf{k} \right)$ are, in the frequency representation,

\[
\left[ i \omega - \tilde{E} (\mathbf{k}) \right] \tilde{G} _{\sigma} \left( \mathbf{k} \right) - \Delta \tilde{F} _{\sigma} \left( \mathbf{k} \right) = \frac{\Delta}{2} E \left( \mathbf{E}_{\text{kin}} \left( \mathbf{k} \right) \right),
\]

\[
\tilde{E} \left( \mathbf{E}_{\text{kin}} \left( \mathbf{k} \right) \right) = \frac{\Delta \left( \mathbf{E}_{\text{kin}} \left( \mathbf{k} \right) \right)}{2}, \quad \mathbf{E} = \frac{\Delta}{2} E \left( \mathbf{E}_{\text{kin}} \left( \mathbf{k} \right) \right).
\]

(8)

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

\[
\mathbf{M} = - T \sum \int \frac{d \mathbf{k}}{2 \pi} \text{Sp} \left[ \tilde{G} _{\sigma} \left( \mathbf{k} \right) (\mathbf{e} \cdot \mathbf{h}) \tilde{G} _{\sigma} \left( \mathbf{k} \right) + \tilde{F} _{\sigma} \left( \mathbf{k} \right) (\mathbf{e} \cdot \mathbf{h}) \tilde{F} _{\sigma} \left( \mathbf{k} \right) \right],
\]

(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

\[
\tilde{G} _{\sigma} \left( \mathbf{k} \right) = \frac{1}{2} \sum \left( 1 + \sigma \mathbf{e} \right) G_{\sigma} \left( \mathbf{k} \right), \quad e = \frac{E \left( \mathbf{E}_{\text{kin}} \left( \mathbf{k} \right) \right)}{ | E \left( \mathbf{E}_{\text{kin}} \left( \mathbf{k} \right) \right) |}
\]

\[
\tilde{F} _{\sigma} \left( \mathbf{k} \right) = \frac{1}{2} \sum \left( 1 + \sigma \mathbf{e} \right) F_{\sigma} \left( \mathbf{k} \right), \quad \mathbf{e} = \pm 1, \quad n = \frac{k}{k_F}.
\]

(10)

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

\[
G_{\sigma} \left( \mathbf{k} \right) = \frac{i \omega + E \left( \mathbf{k} \right)}{\omega^2 + \Delta^2 + E \left( \mathbf{k} \right)^2}, \quad F_{\sigma} \left( \mathbf{k} \right) = \frac{\Delta}{\omega \Delta + E \left( \mathbf{k} \right)^2}, \quad E \left( \mathbf{k} \right) = -E \left( -\mathbf{k} \right) + | E \left( \mathbf{E}_{\text{kin}} \left( \mathbf{k} \right) \right) | \cdot \mathbf{e}.
\]

(11)

It follows from (9) and (10) that the expression for the paramagnetic moment $\mathbf{M}$ can be written in the form

\[
\mathbf{M} = - T \sum \int \frac{d \mathbf{k}}{2 \pi} \left[ \frac{1}{2} (1 - \mathbf{e} \cdot \mathbf{e}) \left[ G_{\sigma} \left( \mathbf{k} \right) G_{\sigma} \left( -\mathbf{k} \right) + F_{\sigma} \left( \mathbf{k} \right) F_{\sigma} \left( -\mathbf{k} \right) \right] \right].
\]

(12)

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

\[
\chi(\mathbf{n}) = \frac{1}{2} \mathbf{e} \cdot \mathbf{e} \int d E \left( \mathbf{k} \right) \sum_{\sigma, \sigma', \sigma''} \left[ G_{\sigma} \left( \mathbf{k} \right) G_{\sigma'} \left( \mathbf{k} \right) + F_{\sigma} \left( \mathbf{k} \right) F_{\sigma'} \left( \mathbf{k} \right) \right],
\]

(13)

where $\chi_e$ is the paramagnetic susceptibility of the metal in the normal state. Then the expression for $\mathbf{M}$ can be represented in the form

\[
\mathbf{M} = \int d \mathbf{n} \chi(\mathbf{n}) \mathbf{e} \left( \mathbf{n} \right) \left[ \chi_e(\mathbf{n}) - \chi(\mathbf{n}) \right].
\]

(14)

The quantity $\chi_e$ does not depend on the spin–orbit interaction and is equal to the paramagnetic susceptibility $\chi_0$ of an ordinary superconductor.

We integrate with respect to energy in the expression for $\chi_e(\mathbf{n})$, assuming the $E_\mathbf{n} \left( \mathbf{E}_{\text{kin}} \right)$ spectrum to be isotropic and $\epsilon_0 << E_\mathbf{n} \left( \mathbf{E}_{\text{kin}} \right)$ in a pyroelectric and $\mathbf{E} = (k_x, k_y, k_z)$ in a layered compound. Then

\[
\chi_e(\mathbf{k}) = \chi_0 \left[ 1 - \frac{\pi T \Delta^2}{\epsilon_0} \sum \frac{1}{\epsilon_0 + \Delta^2 \epsilon_0} \right],
\]

(15)

As $T \rightarrow 0$ we obtain

\[
\chi_e(0) = \chi_0 \left[ 1 - \frac{\pi T \Delta^2}{\epsilon_0} \sum \frac{1}{\epsilon_0 + \Delta^2 \epsilon_0} \right], \quad \chi_e(0) = 0.
\]

(16)

Let us determine the character of the angular dependence of the susceptibility for a pyroelectric superconductor in the case when the field $\mathbf{H}$ is directed at an arbitrary angle relative to the polar axis. Recognizing that the quantities $\chi(\mathbf{n})$ depend only on the angle $\theta$ 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 $\langle \epsilon \epsilon' \rangle = \frac{1}{2} \delta_{ij}$ for $\langle \epsilon \epsilon' \rangle = 0$ if $i \neq z$ or $j = z$ (the $z$ axis is chosen to be the polar axis). Taking this into account, the expression (14) becomes

\[
\mathbf{M} = \int \frac{d \mathbf{n}}{4 \pi} \chi(\mathbf{n}) \mathbf{e}(\mathbf{n}) \left[ \chi_e(\mathbf{n}) + \frac{1}{2} \chi(\mathbf{n}) \right] \left[ \mathbf{H} - \mathbf{a}(\mathbf{n}) \right] / \left[ H - a(\mathbf{n}) \right],
\]

(18)

Bulaevskii et al.

where \( \mathbf{a} \) is a unit vector along the polar axis.

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

\[
\chi_{a} = \chi_{a} \left\{ \frac{1}{T} \sum_{\mathbf{e}, \mathbf{r}} \frac{1}{1 + (a \sin \theta)^2} \right\},
\]

\[
\chi_{a} = \frac{i}{x T} \frac{1}{2 \pi} \int_{0}^{2\pi} d\theta \frac{1}{1 + (a \sin \theta)^2} \ln \left( \frac{\sin \theta}{\sin \theta + a} \right),
\]

\[
\chi_{a} = \frac{i}{x T} \frac{1}{2 \pi} \int_{0}^{2\pi} d\theta \frac{1}{1 + (a \sin \theta)^2} \ln \left( \frac{\sin \theta}{\sin \theta + a} \right).
\]

At \( T = 0 \) we have

\[
\chi_{a} = \chi_{a} \left\{ \frac{1}{T} \sum_{\mathbf{e}, \mathbf{r}} \frac{1}{1 + (a \sin \theta)^2} \right\},
\]

\[
\chi_{a} = \frac{i}{x T} \frac{1}{2 \pi} \int_{0}^{2\pi} d\theta \frac{1}{1 + (a \sin \theta)^2} \ln \left( \frac{\sin \theta}{\sin \theta + a} \right),
\]

where \( \alpha = \epsilon_{1}/\Delta \). At \( \alpha \gg 1 \) we obtain

\[
\chi_{a} = 1 - \frac{1}{2} \ln \left( \frac{\alpha}{\alpha} \right), \quad \chi_{a} = \frac{1}{2}.
\]

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) \( \langle \chi \rangle = (2 \chi_{a} + \chi_{b})/3 \). At \( \epsilon_{1} \gg \Delta \) we have \( \langle \chi \rangle = \frac{2}{3} \chi_{a} + \frac{1}{3} \chi_{b} \), 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 \( \omega \) and the gap \( \Delta \) by the quantities \( \tilde{\omega} = \eta \omega \) and \( \tilde{\Delta} = \eta \Delta \), where \( \eta = 1 + 1/2 \), \( \nu = 1/2 \), and \( \tau \) 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 \( \tilde{J} \) and of the Green's functions in the Nambu matrix representation.

For the vertex part \( \tilde{J}_{0} \) of zeroth order in the impurities and for the Green's function \( \tilde{S} \) of the electron we have in the Nambu representation

\[
\tilde{J}_{0} = \text{const}, \quad \tilde{S} = \frac{1}{2} \sum_{i=1}^{3} (1 + i \omega) G_{ii},
\]

In the ladder approximation we obtain for \( \tilde{J} \) the equation

\[
\tilde{J} = \tilde{J}_{0} + \frac{1}{4} \sum_{k, \kappa} (1 + i \omega) (G_{ii} + G_{kk}) (1 + \tilde{s} \omega).
\]

The magnetic moment is expressed in terms of the Green's function and the vertex part \( \tilde{J} \) with the aid of the expressions

\[
M = \tau \sum_{i=1}^{3} S_{i} \tilde{J}_{i} = -\tilde{J} \tilde{S} \tilde{J}.
\]

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

It is seen from (22) that in the case of isotropic scattering by the impurities \( \tilde{J} \) depends only on the frequency \( \omega \) and does not depend on the momentum. The preferred direction in the dependence of \( \tilde{J} \) on the spin matrices is therefore governed only by the magnetic field. The solution of (22) can then be sought in the form \( \tilde{J} = \sigma \cdot h_{0} \tilde{\gamma} \), where \( h_{0} \) is the vector of the magnetic-field direction, and \( \gamma \) depends only on \( \omega \) and is determined from the equation

\[
\gamma(\omega) = \gamma_{0} + \frac{1}{4} \sum_{k, \kappa} (1 + \tilde{s} \omega) S_{i1}(\kappa) \gamma(\omega) S_{i1}(\kappa), \quad \gamma_{0} = \hbar \tilde{h}_{0} \hbar \left( \begin{array}{c} 1 \\ 0 \\ 0 \\ 1 \end{array} \right).
\]

For \( \gamma_{0} \) we obtain

\[
\chi_{l} = \frac{1}{T} \sum_{\mathbf{e}, \mathbf{r}} \frac{1}{1 + (a \sin \theta)^2} \ln \left( \frac{\sin \theta}{\sin \theta + a} \right),
\]

\[
\chi_{l} = \frac{i}{x T} \frac{1}{2 \pi} \int_{0}^{2\pi} d\theta \frac{1}{1 + (a \sin \theta)^2} \ln \left( \frac{\sin \theta}{\sin \theta + a} \right).
\]

From (24) follows an equation for \( \tilde{S} \) in the form

\[
\tilde{S}(\omega) = \hbar \tilde{P}_{l}(\omega) + \frac{1}{2} \sum_{k, \kappa} (1 + \tilde{s} \omega) S_{i1}(\kappa) \tilde{S}(\omega) S_{i1}(\kappa), \quad \tilde{P}_{l}(\omega) = \frac{1}{4} \sum_{k, \kappa} (1 + \tilde{s} \omega) S_{i1}(\kappa) \tilde{P}_{l}(\omega) S_{i1}(\kappa).
\]

Summing over the momenta in the expression for \( \tilde{P}_{l}(\omega) \), we obtain

\[
\tilde{P}_{l}(\omega) = \tilde{P}_{l}(\omega) \tau_{l} + \tilde{P}_{l}(\omega) \tau_{l}, \quad \tau_{l} = \left( \begin{array}{c} 0 \\ 1 \\ -1 \\ 0 \end{array} \right).
\]

The solutions for \( \tilde{P}_{l}(\omega) \) have the same matrix form as \( \tilde{P}_{l}(\omega) \), i.e.,

\[
\tilde{P}_{l}(\omega) = \Pi_{l}(\omega) \tau_{l} + \Pi_{l}(\omega) \tau_{l}, \quad \Pi_{l}(\omega) = \left( \begin{array}{c} 0 \\ 1 \\ -1 \\ 0 \end{array} \right).
\]

and for the quantities \( \Pi_{l}(\omega) \) and \( \Pi_{l}(\omega) \) we have the system of algebraic equations

\[
\Pi_{l}(\omega) = \Pi_{l}(\omega) \tau_{l} + \Pi_{l}(\omega) \tau_{l}, \quad \Pi_{l}(\omega) = \left( \begin{array}{c} 0 \\ 1 \\ -1 \\ 0 \end{array} \right).
\]

The problem has been reduced to summation over the momenta in the expressions for \( \tilde{P}_{l}(\omega) \) 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 \( \varphi \). Integration with respect to energy in the expressions for \( \tilde{P}_{l} \) and \( \tilde{P}_{l} \) can be carried out between infinite limits. The integration with respect to \( E_{0} \) in the expression for \( \tilde{P}_{l} \) will be represented in the form of the difference between the integral \( J_{2} \) from \( -\infty \) to \( +\infty \) and the integral \( J_{1} \) from \( -\infty \) to \( -E_{0} \). When the second integral \( J_{1} \) is substituted in the expression for \( \chi_{l} \), we obtain the susceptibility of the metal in the normal state. The quantities \( \tilde{P}_{l} \), \( \tilde{P}_{l} \), and \( J_{1} \) take the form

\[
\tilde{P}_{l}(\omega) = \frac{1}{4} \sum_{k, \kappa} (1 + \tilde{s} \omega) S_{i1}(\kappa) \tilde{P}_{l}(\omega) S_{i1}(\kappa) - \tilde{P}_{l}(\omega) \tau_{l} + \tilde{P}_{l}(\omega) \tau_{l}, \quad \tilde{P}_{l}(\omega) = \left( \begin{array}{c} 0 \\ 1 \\ -1 \\ 0 \end{array} \right).
\]
FIG. 1. Levels of constant values of the relative magnetic susceptibility $\chi_{\alpha}/\chi_s$ for layered superconductors as functions of the parameters $\lambda/\alpha = 1/2 \pi \kappa_1$ and $\alpha = \kappa_1/\Delta(0)$.

$P_{\alpha} = \frac{2n\alpha^2}{\Omega^2 (\Omega^2 + \kappa_0^2)}, \quad P_{\lambda} = -\frac{\pi \kappa_1}{\Omega^2 (\Omega^2 + \kappa_0^2)},$ (30)

$J_1 = \frac{\kappa_1}{\Omega^2 (\Omega^2 + \kappa_0^2)}, \quad \tilde{\Omega} = \tilde{\kappa} + \Delta^*.$

We ultimately obtain

$$\frac{\chi_{\lambda}(T)}{\chi_s} = 1 - n \frac{\alpha}{\lambda} \sum_{\omega} \frac{1}{(\omega^2 + \lambda^2)^{1/2} + \omega},$$ (31)

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

$$\frac{\chi_{\lambda}(0)}{\chi_s} = 1 - \frac{\alpha}{\lambda} \frac{dx}{[\cos x + \alpha^2]^{1/2}}, \quad \lambda = \frac{\nu}{\Delta(0)}, \quad \alpha = \frac{\kappa_1}{\Delta(0)}.$$ (32)

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

$$\frac{\chi_{\lambda}(0)/\chi_s}{\chi_s} = 1 - \frac{\alpha}{\lambda} \frac{dx}{[(\kappa + \sec x)^2 + \alpha^2]^{1/2}}, \quad \lambda = \frac{\nu}{\Delta(0)}, \quad \alpha = \frac{\kappa_1}{\Delta(0)}.$$ (33)

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

$$\frac{\chi_{\lambda}(0)/\chi_s}{\chi_s} = 1 - \frac{\alpha}{\lambda}, \quad \alpha \gg \lambda.$$ (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 $H_{\alpha}^c$ of a superconductor under the assumption that there is no orbital effect at all ($H^c_{\alpha} = \infty$) and that the transition from the normal state to the superconducting state is of second order. Then the upper critical field $H_{\alpha}^c$, which is determined by the paramagnetic effect, is determined from Eq. (9) subject to the condition $\Delta = 0$. With allowance for the scattering by the impurities, we obtain the equation

$$1 = \frac{1}{2} Sp \sum_{\omega} \langle G_{\omega, \lambda} \rangle \sigma_{\alpha}^* \sigma_{\alpha}^\dagger.$$ (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

$$\langle \tilde{G}_{\omega, \lambda}(r, r') \rangle = \langle \tilde{G}_{\omega, \lambda}(r, r') \rangle \otimes \tilde{G}(r, r'),$$ (36)

and the Green's function $\langle \tilde{G}_{\omega, \lambda}(r, r') \rangle$, 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 $\omega$ by $\omega + \nu \text{sign} \omega$. Equations (35)–(37) are transformed into

$$1 = \frac{1}{2} \lambda \sum_{\omega_{\alpha, \lambda}, \omega_{\alpha, \lambda}} \langle \tilde{G}_{\omega_{\alpha, \lambda}} \rangle \langle \tilde{G}_{\omega_{\alpha, \lambda}} \rangle \otimes \tilde{G}(k),$$ (38)

where $G^*$ is the Hermitian adjoint of $G$ and is obtained from $G$ by replacing the operator $\sigma$ by $-\sigma$.

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

$$B = \left( \omega + \omega^* \right) \left( \omega^* + \omega^* + v \right)^{1/2},$$ (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 $A = 1/(2T\tau_0)$ for different values of the spin-orbit interaction parameter $\alpha = \epsilon_1/\Delta(0)$: a) $\alpha = 3$, b) $\alpha = 5$, c) $\alpha = 7$.

and at $\nu = 0$ we have the previously obtained equation[11].

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

$$B = e_1(\omega^2 + h^2 + \epsilon_1^2)^\gamma \ln \left( \frac{1 + \epsilon_1^2}{(\omega^2 + h^2)^\gamma} \right)^\nu + \frac{e_1}{(\omega^2 + h^2)^\gamma}.$$

(43)

At $\nu = 0$ and as $\omega \to 0$ we have $h^2B^2 < 1$, 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 $e_1$ in pyroelectrics. The field $h_{ps}$ remains finite in the presence of impurities, and also at $T > 0$.

At $\nu \gg \epsilon_1^2$, accurate to terms $(\epsilon_1/\nu)^2$, we have

$$\ln \frac{T^2}{T} = 2nT \sum \frac{h^4}{\omega^4 + h^2 + c\epsilon_1(\omega/\nu)},$$

(44)

where $C = \frac{1}{2}$ for layered systems and $\frac{3}{2}$ 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 $\lambda \sim \alpha^2$.

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

$$h_{ps}^*(T) = \frac{q}{\pi} (T_c - T) \left( (\epsilon_1^2 + \nu)^\gamma - \nu \right).$$

(45)

Figures 2a, 2b, and 2c show the temperature dependence of $H_{ps}/H_p$ at various values of the parameters $\alpha$ and $\lambda$. At $\lambda = \alpha^2$, the slope of the plot of $H_{ps}$ 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 $\lambda$ and $\alpha$ 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 $\epsilon_1 - B\rho_0$, where $\rho$ 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 $\rho \sim V_{B2}/V_{B1}(\Delta E)^2$). In spin-orbit scattering, the characteristic energy is $h/\tau_{so} = \beta h\nu \sim n\beta^2 \cdot V_{B2}/E_F$, where $\tau_{so}$ 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 $\beta$), 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.
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 critical field $H^*_{op}$ is strong enough in comparison with $H_p = H_{c2}(H^*_p - H_p)$. In bulky weakly anisotropic superconductors $H^*_p$ 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 satisfied under the rather stringent requirements $c^2/T^* \gg \nu' > m
u^2$, 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 $H^*_p > H_p$ 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 pyroelectro-superconductor samples would be of great interest. The paramagnetic limit $H^*_p$ is in this case maximal in a field parallel to the polar axis, and the quantity $H^*_p$ for this field direction is determined by Eqs. (41) and (43).

In strongly anisotropic systems, at definite directions of the magnetic field, the condition $H^*_p > H_p$ 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 $H^*_p$, determined from the data obtained for $-8H_{c2}(H^*_p - H_p)$, is approximately 120 kOe, while $H_p = 130$ kOe ($T_c = 7.5$ K). At $1.5K$, experimental yields $H_{c2} = 130$ kOe and no lowering $H^*_p$, on account of the paramagnetic effect is observed (the ordinary paramagnetic effect would yield for $2H-NbSe_2$ at $T = 0$ a value of $H^*_p$ smaller by a factor 1.5-2 than $H^*_p$). In $2H-NbSe_2$, as noted in Sec. 1 above, an incommensurate CDW structure is observed, and according to the estimates of Schwab et al. we have $\lambda = 1$. It is therefore not excluded, in principle, that the suppression of the influence of the paramagnetic effect on $H_{c2}$ 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 $H^*_p$ is practically unlimited, $\geq 200$ kOe, and $H^*_p > 60$ kOe ($T_c = 3.2$ K). 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 over the paramagnetic limit in this compound can therefore be attributed to spin-orbit interaction of the electrons with the lattice.

It appears that another possible mechanism of suppressing the paramagnetic effect may be spin-orbit interaction of the electrons with impurities only. Klemm et al. emphasized that to explain the experimental data on $TaS_2(Py)_{1/2}$ it is necessary to have $\tau_0 < 5 \times 10^{-14}$ sec (at $T = 0$ we have $H_{c2} = 0.602(\tau_0 T_c)^{1/2} H_p$). If we assume $\tau_0 = 10^7$ ($\beta = 0.3$), then the value of $\tau$ turns out to be very small, but still acceptable (optical investigation yield for compounds with $TaS_2(Py)_{1/2}$ an electron optical scattering time $\tau \approx 4 \times 10^{-14}$ 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 $\phi$ and $\phi'$ of the waves.

$$F = F_1 + F_2,$$

$$F_1 = \int d\alpha (\alpha^2 + \beta \alpha^3 + \gamma \alpha^4 - \delta \alpha^2 - \epsilon \alpha^3 - \zeta \alpha^4 - D \alpha^2 - E \alpha^3 - F \alpha^4),$$

where $F_1$ contains gradient terms of no importance to us, and $\alpha$, $\beta$, and $\delta$ have the same coordinate dependence as $\alpha$. From (A.1) we obtain for the free-energy terms that depend on the phase shifts $\phi$ and $\phi'$:

$$F(\phi, \phi') = F_1 - \frac{3}{2} b_1 u_1 u_1 \cos \phi - \frac{1}{4} b_1 \sum u_i^2, \cos \gamma_i,$$

$$+ \frac{1}{4} c_1 u_1 u_1 \sum \cos (-\phi + \gamma).$$

The minimum of $F$ is reached at $u_1 = u$ and $v_1 = v$. It follows also from (A.2) that the minimum of $F$ is reached at $\gamma = \gamma$. The phase shifts $\phi$ and $\gamma$ are determined from the equations

$$A \sin \phi + B \sin (-\phi + \gamma) = 0, \quad A = \beta, B = \gamma, C = \alpha, D = \phi,$$

$$\sin \gamma = \gamma = 0,$$

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

$$F = F_1 - A(-1)^n - B(-1)^m + D(-1)^m,'$$

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

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

with energy
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.

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

(A.6)


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