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The Ginzburg–Landau equation for superconductors of polar symmetry

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Abstract. The superconductivity of metals whose symmetry group includes a polar axis is considered. A modified Ginzburg–Landau free-energy functional is derived, and it is shown that due to the absence of space parity the free-energy density involves an additional term of the form $-\frac{1}{2}\kappa(\boldsymbol{c} \times B) \cdot (\Psi^* \boldsymbol{\Pi} \Psi + \Psi \boldsymbol{\Pi}^* \Psi^*)$ where Ψ is the order parameter, $\boldsymbol{\Pi} = -\mathrm{i}\boldsymbol{\nabla} - (2e/c)\boldsymbol{A}$, $\boldsymbol{c}$ is the unit vector along the polar axis, $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$, and κ is a real function of the electronic structure parameters. The consequences of the term on the problem of the critical current in a thin single-crystalline film are studied, and an anomalous effect of the magnetic field on the value of the current is predicted: namely, if the film is produced in such a way that its plane is perpendicular to the vector $\boldsymbol{c}$, then the magnitude of the critical current $J_c(\boldsymbol{B})$ should depend on the sign of the mixed product $(\boldsymbol{c} \times B) \cdot \hat{\boldsymbol{J}}_c$, i.e., the critical current should be different for two opposite directions.

1. Introduction

Among the great number of superconducting materials discovered recently, a group of inorganic metals is somewhat exceptional. These are intermetallic compounds whose symmetry group includes a polar axis. Examples of the metals in this as yet relatively small group include some of the ternary silicides [1] ($CeCoSi_3$ and probably $LaRhSi_3$ and $LaIrSi_3$) with space group $I4mm$. The group, however, should extend as new superconductors of complex composition are synthesized and investigated. Indeed, if the elementary cell of a compound contains many different ions, there is no reason for their arrangement to always be centrosymmetrical.

Central symmetry of a metal may also be violated as a result of a structural phase transition as was suggested for the first time in a paper by Anderson and Blount [2], on work in connection with phase transformations in A15- (β-tungsten-) structure superconductors. It was argued in [2] that if the structural transition, which takes place at temperature T_M somewhat above the superconducting transition T_c, is of second order, then it should be accompanied by an internal symmetry change, such as the loss of the inversion centre or even development of a polar axis, in addition to the change in lattice size and shape. This prediction proved to be correct—'ferroelectric' metals (e.g. V_2Hf with space group $Imm2$ [3]) were subsequently discovered. Furthermore, polar superconductors might be manufactured by means of the MBE technique.

The consequences of the absence of central symmetry for the superconducting properties were not discussed in [2]. It is clear, however, that the presence of a polar axis can have an effect on the Cooper pairing. One consequence follows directly from pure symmetry considerations. It is the appearance of the invariant $\boldsymbol{q} \cdot (\boldsymbol{c} \times \boldsymbol{B})$ (allowed by the polar

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symmetry) in the dynamical characteristics of a Bose-type excitation inherent in a given polar compound. Here $\boldsymbol{q}$ is the wave vector of the excitation, the unit vector $\boldsymbol{c}$ points to the polar axis, and $\boldsymbol{B}$ is an external magnetic field. The invariant was first met in semiconductor optics [4, 5], when a correction to the energy of an exciton, even in the exciton momentum and the magnetic field, was detected in CdS crystals. Later on, the invariant appeared in the problem of the conduction electron spin resonance in doped polar semiconductors. It was shown that the spin-density fluctuation of the wave vector $\boldsymbol{q}$ decays with a rate which depends on the field $\boldsymbol{B}$ and $\boldsymbol{q}$ through the invariant [6, 7]. A relevance of the invariant to the Cooper instability in strict two-dimensional systems (forming the superfluid condensate with a non-zero phase) was mentioned in [8]. On the grounds of all that has been said, one can expect the invariant to play an appreciable role in superconducting problems with the spatially varying order parameter in the Ginzburg–Landau (GL) region as well.

The purpose of this paper is to develop a modification of the GL theory suitable for three-dimensional polar metals and, with the help of the theory, to investigate the influence of an external magnetic field on the critical current of a thin film. The polar symmetry enters into the problem under discussion through the spin–orbit (SO) term in the one-particle Hamiltonian

$$H_{so} = \frac{\alpha}{\hbar}(\boldsymbol{p} \times \boldsymbol{c}) \cdot \boldsymbol{\sigma} \tag{1.1}$$

where $\boldsymbol{p}$ is the electron momentum, $\boldsymbol{\sigma}$ is the Pauli spin matrix-vector, and α is the SO constant. The SO term was discussed for the first time in connection with the energy spectrum of bulk [9] and surface [10] electronic states in certain semiconductors. The origin of the term becomes clear if one writes down an equation expressing the term as a third-order perturbation theory term of the form [6]

$$\frac{\alpha}{\hbar}(\boldsymbol{p} \times \boldsymbol{c}) \cdot \boldsymbol{\sigma} = \sum_n \langle c| \frac{\hbar}{m}\boldsymbol{p} \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} |n\rangle \frac{(n|\zeta \boldsymbol{l} \cdot \boldsymbol{\sigma}|n)}{(E_n - E_c)^2} (n|eE\boldsymbol{c} \cdot \boldsymbol{r}|c) \tag{1.2}$$

where $|c\rangle$ refers to the conduction band, the sum is over the other appropriate bands, ζ is the SO coupling in the nth band, and E is the magnitude of the average odd intracrystalline electric field. The field does not vanish due to the polar symmetry of the lattice and cannot be completely screened out by free electrons. Although equation (1.2) was derived in [6] for semiconductors, i.e. under the assumption that the volume of momentum space enclosed by the Fermi surface is much less than that of the Brillouin zone and the parameter $pa/\hbar$ (a is the crystal lattice constant) of $\boldsymbol{k} \cdot \boldsymbol{p}$ perturbation theory [11] is small, one may believe that it is also applicable to metals, where $p_F a/\hbar \simeq 1$, at least as an order-of-magnitude estimate. An important point of (1.2) is that the contribution of the nth band (to the constant α of the conduction band) is proportional not only to the magnitude of the SO energy ζ of the atoms that the nth band is built from, but also to the inverse square of the energy gap $E_c - E_n$. If the gap is small on the atomic scale (Ryd = 27 eV), then this factor can compensate the smallest of ζ and strongly enhance α.

Our main result reads as follows. In the presence of H_{so}, the GL free energy

$$\Omega(\psi, \psi^*) = \int \mathrm{d}^3 r \left[\frac{1}{\eta} \left(\frac{T - T_c}{T_c} |\psi|^2 + \frac{1}{2n}|\psi|^4 \right) + \frac{1}{4m} (\boldsymbol{\Pi}^* \psi^*) \cdot (\boldsymbol{\Pi}\psi) \right. \\ \left. - \frac{1}{2}\kappa (\boldsymbol{c} \times \boldsymbol{B}) \cdot (\psi^* \boldsymbol{\Pi} \psi + \psi \boldsymbol{\Pi}^* \psi^*) \right] \tag{1.3}$$

has, as well as conventional terms, an anomalous P-odd term. Here $\mathbf{\Pi} = -\mathrm{i}\boldsymbol{\nabla} - (2e/c)\boldsymbol{A}$, $\boldsymbol{A}$ is the vector potential, $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$, m is the electron mass, $\eta = 7\zeta(3)mv_F^2/12(\pi T_c)^2$, $\zeta(n)$ is the Riemann ζ function, v_F is the Fermi velocity, $n = p_F^3/3\pi^2$ is the electron density, and the constant κ incorporates the SO constant α and the Bohr magneton μ_B in the form

$$\kappa = 3\frac{\alpha}{v_F} f_3\left(\frac{\alpha p_F}{\pi T_c}\right)\frac{\mu_B}{p_F} \tag{1.4}$$

where

$$f_3(x) = \frac{4}{7\zeta(3)} \int_0^{\pi} \mathrm{d}t \sin t \sum_{n\geq 0} \frac{(x \sin t)^2}{(2n+1)^3[(2n+1)^2 + (x \sin t)^2]}. \tag{1.5}$$

In equation (1.3) and below, the Boltzmann constant k_B and Planck's constant $\hbar$ are set to unity. It is not difficult to discern the invariant $(\boldsymbol{c} \times \boldsymbol{B}) \cdot \boldsymbol{q}$ in the last term of equation (1.3). Several remarks are in order. (i) The SO constant α enters the problem in two ways. The parameter $\delta = \alpha p_F/\epsilon_F$ is certainly very small. Another parameter $\alpha p_F/\pi T_c$ is much greater than δ and can be of the order of unity in real substances. Here we take $\alpha p_F/\pi T_c \simeq 1$ and consequently $f_3 \simeq 1$. (ii) Equation (1.3) suggests s-type pairing. Strictly speaking, in the presence of H_{so}, the order parameter contains a small fraction of a triplet state [8]. The account of this fraction does not bring about qualitative changes in the conclusions obtained. Therefore, to avoid unnecessary complexities obscuring the main idea, the triplet part of the order parameter will be neglected. (iii) It should be noticed that if, due to electronic correlations, the paramagnetic susceptibility of the normal state χ_n is strongly enhanced as compared with that of free electrons, then the same strengthening factor should be added in equation (1.4) for the constant κ.

The additional term in the GL free energy should obviously reveal itself in P-odd effects in a current-carrying sample. We shall show that the magnitude of the critical current J_c, in a film of thickness less than both the penetration depth and the coherence length $\xi(T)$ and subjected to a weak parallel magnetic field $\boldsymbol{B}$, has the form

$$J_c(\boldsymbol{B}) = J_c(0)\left[1 + (\boldsymbol{c} \times \boldsymbol{B}) \cdot \hat{\boldsymbol{J}} f_3\, \delta \frac{3(7\zeta(3))^{1/2}}{8H_{c2}p_F\xi(T)}\right] \tag{1.6}$$

where $\hat{\boldsymbol{J}}$ is the unit vector along the supercurrent, $H_{c2} = c/(2e\xi^2(T))$, $\xi(T) = \xi_0(T_c/(T_c - T))^{1/2}$, and $\xi_0 = v_F/2\pi T_c$. One can assume that equation (1.6) is approximately valid at $B \sim H_{c2}$ and $T - T_c \sim T_c$ as well. In this region, the main small parameter is $\delta(p_F\xi_0)^{-1} = \delta(\pi T_c/\epsilon_F)$. Neither the value of α nor the precise electronic band structure is known for polar superconductors at present. Some crude estimates and an analogy with pyroelectric CdS, where equation (1.2) was established to work very well [6], allow one to expect the relative magnitude of the effect to be of the order of 10^{-4}–10^{-3} under favourable conditions (i.e. small Fermi energy, large paramagnetic susceptibility, and large atomic numbers of the elements composing the metal). One way of detecting the effect is to study the influence of the magnetic field reversal on the state of the film. If, with the negative sign of $\alpha(\boldsymbol{c} \times \boldsymbol{B}) \cdot \hat{\boldsymbol{J}}$, the supercurrent has a nearly critical magnitude (so the difference between the real value of the current and the critical one is within the very small region mentioned above), then the magnetic field reversal should drive the film into the normal state. The results we have given are for clean metals, when $T_c\tau \gg 1$ (τ is the mean collision time). An account of impurities presents no difficulty.

The organization of the rest of the paper is as follows. In section 2, a detailed description of the model and the Feynman rules is given. An evaluation of the anomalous P-odd term in the GL free energy is performed in section 3. In section 4, the problem of the critical current in the film is considered. The conclusions are presented in section 5. The appendix demonstrates a technique for working with Feynman's graphs.

2. The model and formulation

For simplicity, we shall assume that the spectrum of the electrons in the absence of H_{so} and the interparticle interaction is isotropic: $\epsilon_0(\boldsymbol{p}) = p^2/2m$. Then the one-particle Hamiltonian of the polar metal under consideration takes the form

$$H_{(00)}(\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} + \alpha(\boldsymbol{p}\times\boldsymbol{c})\cdot\boldsymbol{\sigma}. \tag{2.1}$$

It follows from (2.1) that the thermal Green function of noninteracting electrons with no external fields is

$$G_{(00)\alpha\beta}(\mathrm{i}\epsilon,\boldsymbol{p}) = \Pi^{(+)}_{\alpha\beta}(\boldsymbol{p})G^0_{(+)}(\mathrm{i}\epsilon, p) + \Pi^{(-)}_{\alpha\beta}(\boldsymbol{p})G^0_{(-)}(\mathrm{i}\epsilon, p) \tag{2.2}$$

$$G^0_{(\pm)}(\mathrm{i}\epsilon, p) = [\mathrm{i}\epsilon - \xi_{(\pm)}(p)]^{-1} \qquad \xi_{(\pm)}(p) = \epsilon_{(\pm)}(p) - \mu \tag{2.3}$$

where

$$\epsilon_{(\pm)}(p) = \epsilon_0(p) \pm \alpha p \sin\phi \tag{2.4}$$

and

$$\Pi^{(\pm)}_{\alpha\beta}(\boldsymbol{p}) = \frac{1}{2}[\delta_{\alpha\beta} \pm (\hat{\boldsymbol{p}}\times\boldsymbol{c})\cdot\boldsymbol{\sigma}_{\alpha\beta}]. \tag{2.5}$$

Here ϕ is the angle between the momentum $\boldsymbol{p}$ and the polar axis, and the operator $\hat{\Pi}^{(\pm)}$ is the projector onto a state with a definite helicity (the projection of a spin on the $\boldsymbol{p}\times\boldsymbol{c}$ direction). It is seen from (2.4) that the states of positive and negative helicity acquire different energies. This Green function is the basic tool for subsequent work. The only difference between the diagram techique obtained and the standard one [12] is in the spinor structure of the Green function and the changed form of the velocity operator:

$$\boldsymbol{v}(\boldsymbol{p}) = \mathrm{i}\,[H_{00}(\boldsymbol{p}), \boldsymbol{r}] = \frac{\boldsymbol{p}}{m} + \alpha(\boldsymbol{c}\times\boldsymbol{\sigma}) \tag{2.6}$$

which, besides the usual scalar part, also has a spin component.

As was mentioned in the introduction, we suggest that s-type pairing takes place, i.e.

$$H_{int} = \frac{\lambda_s}{2}\int \mathrm{d}^3r\,[\psi^+_\beta(\boldsymbol{r})g_{\beta\kappa}\psi^+_\kappa(\boldsymbol{r})][\psi_\delta(\boldsymbol{r})g_{\delta\gamma}\psi_\gamma(\boldsymbol{r})] \tag{2.7}$$

where $\hat{g} = \mathrm{i}\sigma_2$, λ_s is the pairing constant, and $\psi_\gamma(\boldsymbol{r})$ is the electron quantized field operator. The Gor'kov equations [13] for the matrix Green function in momentum space

$$\hat{G}_{\alpha\beta}(\boldsymbol{p},\boldsymbol{p}-\boldsymbol{q},\mathrm{i}\epsilon) = \begin{pmatrix} G_{\alpha\beta}(\boldsymbol{p},\boldsymbol{p}-\boldsymbol{q},\mathrm{i}\epsilon) & F_{\alpha\beta}(\boldsymbol{p},\boldsymbol{p}-\boldsymbol{q},\mathrm{i}\epsilon) \\ F^+_{\alpha\beta}(\boldsymbol{p},\boldsymbol{p}-\boldsymbol{q},-\mathrm{i}\epsilon) & -G^{\mathrm{T}}_{\alpha\beta}(-\boldsymbol{p},-\boldsymbol{p}+\boldsymbol{q},-\mathrm{i}\epsilon) \end{pmatrix} \tag{2.8}$$

have the standard form

$$\int \frac{\mathrm{d}^3 q_1}{(2\pi)^3} \hat{L}_{\alpha\gamma}(\boldsymbol{p}, \boldsymbol{p}-\boldsymbol{q}_1)\hat{G}_{\gamma\beta}(\boldsymbol{p}-\boldsymbol{q}_1, \boldsymbol{p}-\boldsymbol{q}) = (2\pi)^3\,\delta(\boldsymbol{q})\,\delta_{\alpha\beta}\,\hat{1} \tag{2.9}$$

where

$$\begin{aligned}\hat{L}_{\alpha\gamma}(\boldsymbol{p}, \boldsymbol{p}-\boldsymbol{q}) = (2\pi)^3\delta(\boldsymbol{q}) &\begin{pmatrix} \mathrm{i}\epsilon\delta_{\alpha\gamma} - H^{(00)}_{\alpha\gamma}(\boldsymbol{p}) & 0 \\ 0 & \mathrm{i}\epsilon\delta_{\alpha\gamma} + H^{\mathrm{T}(00)}_{\alpha\gamma}(-\boldsymbol{p}) \end{pmatrix} \\ &- \begin{pmatrix} H^{ef}_{\alpha\gamma}(\boldsymbol{p}, \boldsymbol{q}) + H^{(Z)}_{\alpha\gamma}(\boldsymbol{q}) & \Delta_{\alpha\gamma}(\boldsymbol{q}) \\ \Delta^{+}_{\alpha\gamma}(\boldsymbol{q}) & -H^{\mathrm{T}(ef)}_{\alpha\gamma}(-\boldsymbol{p}, \boldsymbol{q}) - H^{\mathrm{T}(Z)}_{\alpha\gamma}(\boldsymbol{q}) \end{pmatrix}\end{aligned} \tag{2.10}$$

$$H^{ef}_{\alpha\gamma}(\boldsymbol{p}, \boldsymbol{q}) = -\frac{e}{c}\boldsymbol{v}_{\alpha\gamma}(\boldsymbol{p})\cdot\boldsymbol{A}(\boldsymbol{q}) \qquad H^{Z}_{\alpha\gamma}(\boldsymbol{q}) = \mu_B\boldsymbol{\sigma}_{\alpha\gamma}\cdot\boldsymbol{B}(\boldsymbol{q}) \tag{2.11}$$

$$\Delta_{\alpha\beta}(\boldsymbol{q}) = -\lambda_s g_{\alpha\beta} T \sum_{\epsilon} \int \frac{\mathrm{d}^3 q_1}{(2\pi)^3}\,\mathrm{Tr}[F(\boldsymbol{p}, \boldsymbol{p}-q)\cdot g^{\mathrm{T}}] \tag{2.12}$$

and the superscript T denotes transposition. As usual [14], to obtain the GL equation, one ought to iterate equation (2.9) up to the third order in $\hat{\Delta}$ and then substitute the result into the self-consistency equation (2.12). The equation for $\hat{\Delta}$ obtained in this way can be conveniently represented in the form of the following stationarity condition:

$$\frac{\delta\Omega}{\delta\hat{\Delta}_{\beta\alpha}(\boldsymbol{q})} = 0 \tag{2.13}$$

for the functional

$$\Omega = \frac{1}{4\lambda_s}\int \frac{\mathrm{d}^3 q}{(2\pi)^3}\,\mathrm{Tr}[\hat{\Delta}^{+}(\boldsymbol{q})\hat{\Delta}(\boldsymbol{q})] + \frac{1}{2}\Phi \tag{2.14}$$

where Φ is a functional of $\hat{\Delta}$ defined diagrammatically in figure 1. All that remains is to expand the diagrams of figure 1 into a series in the order parameter gradient and the small external fields $\boldsymbol{A}$ and $\boldsymbol{B}$.

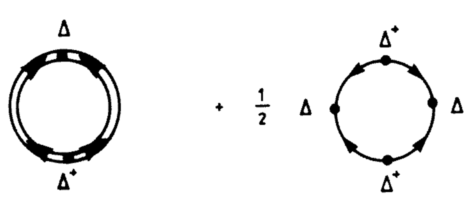

Figure 1. Diagrams which contribute to Φ. The double line with two arrows represents the full Green function of the normal metal which incorporates the external field. The single line represents the bare Green function of equation (2.2). Since, according to the general spirit of the GL expansion, one can neglect the influence of the external field on the the free-energy term proportional to Δ^4, the second graph may be composed of single lines.

3. Expansion of the functional Φ

We now proceed to evaluate the diagrams of figure 1 using some methods from [15]. With no external field and at the zeroth order of the order parameter gradient, the diagrams, together with the first term in equation (2.14), yield the conventional result [12]

$$D(0)\int \mathrm{d}^3r\left[\left(\frac{T-T_c}{T_c}\right)|\Delta(\boldsymbol{r})|^2+\frac{7\zeta(3)}{16\pi^2T_c^2}|\Delta(\boldsymbol{r})|^4\right] \tag{3.1}$$

where $D(0)=mp_F/2\pi^2$. By deriving (3.1), we used the fact that at the s-type pairing

$$\Delta_{\alpha\beta}(\boldsymbol{r})=g_{\alpha\beta}\Delta(\boldsymbol{r}). \tag{3.2}$$

Corrections to equation (3.1) due to H_{so} are negligible, being proportional to δ^2. According to equation (2.10), the vector potential $\boldsymbol{A}$ and the magnetic field $\boldsymbol{B}$ enter the problem via the energy H_{ef} and the Zeeman energy H_Z respectively (see (2.11)). One more perturbation energy is the Doppler energy

$$H_D(\boldsymbol{p},\boldsymbol{q})=\frac{1}{2}\boldsymbol{q}\cdot\boldsymbol{v}(\boldsymbol{p}) \tag{3.3}$$

acquired by the electron of momentum $\boldsymbol{p}$ by interaction with the external field (or with the order parameter) bearing momentum $\boldsymbol{q}$. Since all the Bose-type fields ($\boldsymbol{A}$, $\boldsymbol{B}$, and $\hat{\Delta}$) are assumed to be slowly varying over space the momenta with which they enter the diagram are much smaller than both p_F and ξ_0^{-1}. Therefore, all three energies can be considered as small perturbations. Note that the Doppler energy is the cause of the appearance of the order parameter derivatives which occur in the expansion in two forms:

$$|\boldsymbol{\nabla}\Delta(\boldsymbol{r})|^2 \tag{3.4}$$

and

$$\boldsymbol{J}_0(\boldsymbol{r})=\Delta(\boldsymbol{r})\frac{\boldsymbol{\nabla}}{2\mathrm{i}}\Delta^*(\boldsymbol{r})-\Delta^*(\boldsymbol{r})\frac{\boldsymbol{\nabla}}{2\mathrm{i}}\Delta(\boldsymbol{r}). \tag{3.5}$$

The diagrammatic representation of an expansion of the Green functions in powers of H_{ef}, H_Z, and H_D is shown in figure 2.

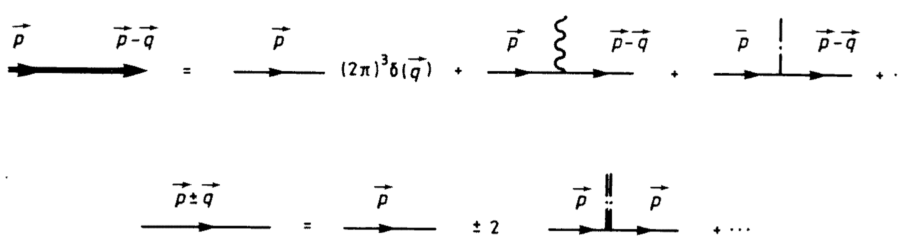

Figure 2. The diagrammatical representation of the perturbation expansion of the full Green function in powers of the electromagnetic, Zeeman and Doppler energies. The wavy line represents a H_{ef} vertex (see equation (2.11)), dash-dot-dash represents a H_Z vertex (see equation (2.11)), double dash-dot-dash represents a H_D vertex (see equation (3.3)).

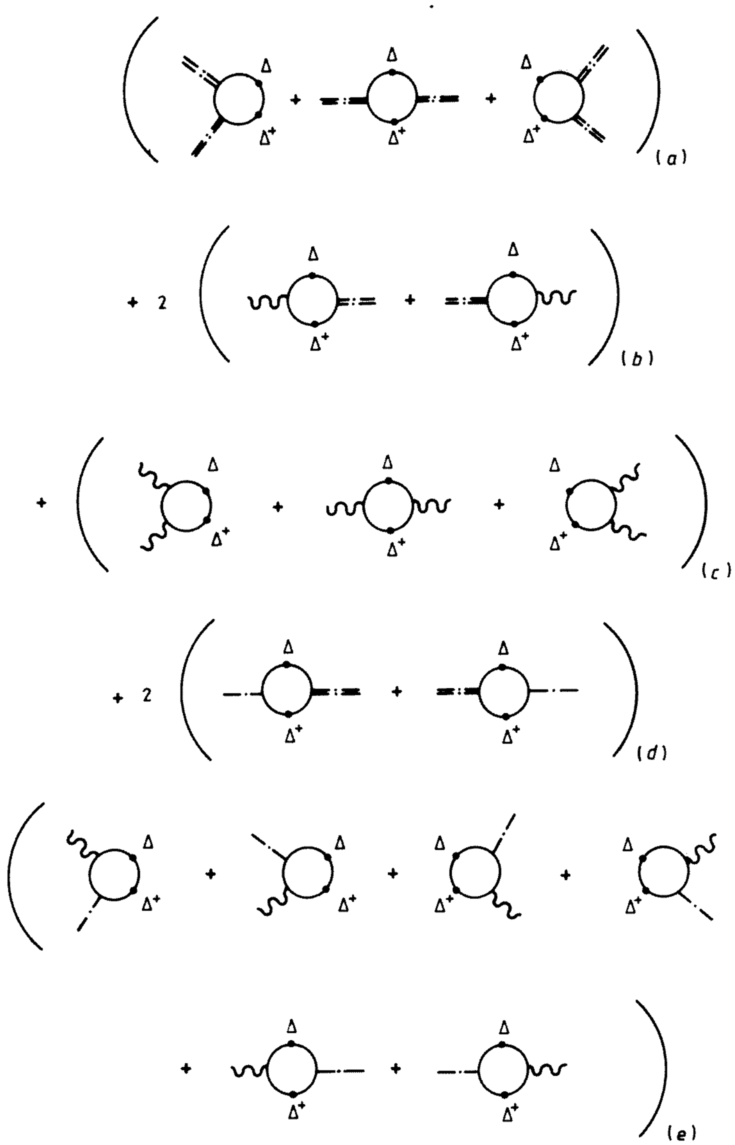

Figure 3. The Feynman graph representation of the expansion of the first diagram of figure 1. The diagrams (*a*), (*b*), and (*c*) contribute to the conventional part of the free energy. The diagrams (*d*) and (*e*) are responsible for the anomalous P-odd part of the free energy.

As usual, only the first diagram of figure 1 should be expanded into a series in powers of the vector potential, the magnetic field, and the order parameter derivatives. The expansion is depicted in figure 3. All the diagrams of figure 3 fall into two classes: the conventional P-even diagrams ((*a*), (*b*), and (*c*)) and the anomalous P-odd ones ((*d*) and(*e*)). One can easily see that evaluation of the conventional graphs does not require H_{so}. Therefore, the Green functions (2.2) take the standard form $\delta_{\alpha\beta}[\mathrm{i}\epsilon - \xi_0(p)]^{-1}$, and we get the well known result [10]

$$2D(0)\int \mathrm{d}^3r\ \frac{\eta}{4m}\left[\boldsymbol{\Pi}\Delta(\boldsymbol{r})\cdot\boldsymbol{\Pi}^*\Delta^*(\boldsymbol{r})\right] \tag{3.6}$$

where η and $\boldsymbol{\Pi}$ are defined after equation (1.3). The evaluation of the anomalous graphs requires a more accurate approach using the exact Green functions of equation (2.2). The way in which the calculation was carrued out is explained in the appendix. As a result, one gets

$$-D(0)\eta\int \mathrm{d}^3r\ \frac{3\alpha}{v_F}f_3\left(\frac{\alpha p_F}{\pi T_c}\right)\frac{\mu_B}{p_F}(\boldsymbol{c}\times\boldsymbol{B}(\boldsymbol{r}))\cdot\left(\boldsymbol{J}_0(\boldsymbol{r})-\frac{2e}{c}\boldsymbol{A}(\boldsymbol{r})|\Delta(\boldsymbol{r})|^2\right). \tag{3.7}$$

By combining equations (3.1), (3.5), and (3.7) and using the function $\psi(\boldsymbol{r})$ defined as

$$\psi(\boldsymbol{r})=\Delta(\boldsymbol{r})\left(\frac{7\zeta(3)}{8(\pi T_c)^2}n\right)^{1/2} \tag{3.8}$$

we obtain equation (1.3). (Note that in the present paper we call both functions, $\psi(\boldsymbol{r})$ and $\Delta(\boldsymbol{r})$, the order parameter.)

4. The critical current

We now consider the suppression of the superconducting state that occurs at large currents. By varying the free-energy functional (1.3) with respect to ψ^* and the vector potential, one gets the GL equations

$$\frac{1}{4m}\left(-\mathrm{i}\boldsymbol{\nabla}-\frac{2e}{c}\boldsymbol{A}\right)^2\psi(\boldsymbol{r})-\kappa(\boldsymbol{c}\times\boldsymbol{B})\cdot\left(-\mathrm{i}\boldsymbol{\nabla}-\frac{2e}{c}\boldsymbol{A}\right)\psi(\boldsymbol{r})$$
$$+\frac{1}{\eta}\left[\frac{T-T_c}{T_c}+\frac{1}{n}|\psi|^2\right]\psi(\boldsymbol{r})=0 \tag{4.1}$$

$$\boldsymbol{J}_s=\frac{e}{m}\left(\boldsymbol{P}_0-\frac{2e}{c}\boldsymbol{A}|\psi|^2\right)-\kappa c\left\{\mathrm{curl}\left[\boldsymbol{c}\times\left(\boldsymbol{P}_0-\frac{2e}{c}\boldsymbol{A}|\psi|^2\right)\right]+\frac{2e}{c}|\psi|^2(\boldsymbol{c}\times\boldsymbol{B})\right\} \tag{4.2}$$

where c is the velocity of light and

$$\boldsymbol{P}_0(\boldsymbol{r})=\psi^*(\boldsymbol{r})\frac{\boldsymbol{\nabla}}{2\mathrm{i}}\psi(\boldsymbol{r})-\psi(\boldsymbol{r})\frac{\boldsymbol{\nabla}}{2\mathrm{i}}\psi^*(\boldsymbol{r}). \tag{4.3}$$

It should be noted that expression (4.2) may also be obtained as a linear response of the current operator

$$\hat{\boldsymbol{j}}=\hat{\boldsymbol{j}}_{kin}+\hat{\boldsymbol{j}}_{dia}+\hat{\boldsymbol{j}}_{par} \tag{4.4}$$

$$\hat{\boldsymbol{j}}_{kin}=\frac{e}{m}\left(\psi^*_\beta\frac{\boldsymbol{\nabla}}{2\mathrm{i}}\psi_\beta-\psi_\beta\frac{\boldsymbol{\nabla}}{2\mathrm{i}}\psi^*_\beta\right)+\frac{e}{m}\alpha\psi^*_\beta(\boldsymbol{c}\times\boldsymbol{\sigma})_{\beta\gamma}\psi_\gamma \tag{4.5}$$

$$\hat{\boldsymbol{j}}_{dia}=-\frac{e^2}{mc}\boldsymbol{A}\psi^*_\beta\psi_\beta\qquad \hat{\boldsymbol{j}}_{par}=-\mu_B c\,\mathrm{curl}(\psi^*_\beta\boldsymbol{\sigma}_{\beta\gamma}\psi_\gamma) \tag{4.6}$$

on the interaction with the electromagnetic field

$$V=-\frac{1}{c}\int \mathrm{d}^3r\ (\hat{\boldsymbol{j}}_{kin}+\hat{\boldsymbol{j}}_{dia})\cdot\boldsymbol{A}+\mu_B\int \mathrm{d}^3r\ (\psi^*_\beta\boldsymbol{\sigma}_{\beta\gamma}\psi_\gamma)\cdot\boldsymbol{B} \tag{4.7}$$

in a way analogous to that of [14].

Suppose that one has a long thin film of thickness d, smaller than both the correlation length $\xi(T)$ and the penetration depth λ, fabricated in such a way that the polar vector $\boldsymbol{c}$ is perpendicular to its plane. The self-field of the current is assumed to be small with respect to the external field $\boldsymbol{B}$, applied parallel to the film. Under these conditions, neglecting corrections of the order of $Bd/H_{c2}\xi$, one may consider $|\psi|$ to be spatially uniform. Hence, the current flows uniformly through the entire cross section of the film. Let us choose a coordinate system $(\hat{\boldsymbol{x}}, \hat{\boldsymbol{y}}, \hat{\boldsymbol{z}})$ such that $\hat{\boldsymbol{x}}$ is parallel to $\boldsymbol{B}$, and $\hat{\boldsymbol{y}}$ to $\boldsymbol{J}$. We look for a solution of equation (4.1) in the form $\psi = |\psi| \exp \mathrm{i}qy$. In the gauge $\boldsymbol{A} = (0, -Bz, 0)$ expression (4.2) for the supercurrent acquires the form

$$\boldsymbol{J}_s = \hat{\boldsymbol{y}} \frac{e}{m} |\psi|^2 \left(q + \frac{2e}{c} Bz \right) \tag{4.8}$$

where the second term in parentheses can also be neglected to the accuracy mentioned above. Then equation (4.1) takes the form of an algebraic equation:

$$\frac{q^2}{4m} - \kappa (\boldsymbol{c} \times \boldsymbol{B}) \cdot \hat{\boldsymbol{J}} q + \frac{1}{\eta} \left[\frac{|\psi|^2}{n} - \left(\frac{T_c - T}{T_c} \right) \right] = 0. \tag{4.9}$$

There will be some maximum value of q, and hence of $\boldsymbol{J}_s$, beyond which one can no longer find a nonzero optimum value of $|\psi|$ to minimize the free energy. This defines J_c. Due to the assumption of homogeneous current flow, the sample will turn abruptly normal when J_s exceeds J_c (by neglecting fluctuations and other subtleties that are not considered here). The simultaneous solution of equations (4.9) and (4.10) presents no difficulties (see [15]). As a result one gets equation (1.6).

5. Summary

In this paper a derivation of the superconducting state properties of the polar metals has been given. To a certain extent, such compounds can be viewed as unconventional superconductors. Due to the lack of inversion centres in the crystal symmetry group, time-reversal symmetry does not ensure the spin degeneracy of the electronic states. The superconductivity in systems with lifted spin degeneracy is still poorly investigated and can be expected to possess unexpected features. Indeed, our study revealed an extra term in the free-energy functional. This term was shown to result in an anomalous magnetic field dependence of the critical current. Still more new interesting effects can be apparently brought out in the nonequilibrium properties of the polar superconductors. So, polar metal superconductivity certainly merits further examination.

Acknowledgments

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Appendix

The subject of this appendix is the method of evaluating the anomalous diagrams encountered in the main text. The calculations can be carried out in a way like that of the Feynman graph calculation in spinor electrodynamics. We shall perform the calculations for one of the diagrams depicted in figure 3(d), because the evaluation of other diagrams is completely analogous.

The contributions of the diagrams are equal and are given by the following expression:

$$T\sum_{\epsilon}\int\frac{\mathrm{d}^3q}{(2\pi)^3}\frac{\mathrm{d}^3q'}{(2\pi)^3}\frac{\mathrm{d}^3p}{(2\pi)^3}\mathrm{Tr}\big\{\hat{G}^{(00)}(\mathrm{i}\epsilon,\boldsymbol{p})\hat{H}_Z(-\boldsymbol{q})\hat{G}^{(00)}(\mathrm{i}\epsilon,\boldsymbol{p}) \times\hat{\Delta}(\boldsymbol{q}'+\tfrac{1}{2}\boldsymbol{q})\hat{G}^{\mathrm{T}(00)}(-\mathrm{i}\epsilon,-\boldsymbol{p})\hat{H}_D(-\boldsymbol{p},\boldsymbol{q}')\hat{G}^{\mathrm{T}(00)}(-\mathrm{i}\epsilon,-\boldsymbol{p})\hat{\Delta}^{+}(\boldsymbol{q}'-\tfrac{1}{2}\boldsymbol{q})\big\}. \tag{A.1}$$

Substituting the Green function (2.2), the Zeeman energy (2.11) and the Doppler energy (3.3) into (A.1) and using the identity

$$-g\boldsymbol{\sigma}^{\mathrm{T}}g^{\mathrm{T}}=\boldsymbol{\sigma} \tag{A.2}$$

gives

$$T\sum_{\epsilon}\int\frac{\mathrm{d}^3q}{(2\pi)^3}\frac{\mathrm{d}^3q'}{(2\pi)^3}\frac{\mathrm{d}^3p}{(2\pi)^3}\sum_{\mu,\nu=+,-}\tfrac{1}{2}\mu_B G^0_{(\mu)}(\mathrm{i}\epsilon,p)G^0_{(\mu)}(-\mathrm{i}\epsilon,p)G^0_{(\nu)}(\mathrm{i}\epsilon,p)G^0_{(\nu)}(-\mathrm{i}\epsilon,p) \times\Delta^*(\boldsymbol{q}'-\tfrac{1}{2}\boldsymbol{q})\Delta(\boldsymbol{q}'+\tfrac{1}{2}\boldsymbol{q})\mathrm{Tr}\big[\hat{\Pi}^{(\mu)}(\boldsymbol{p})(\boldsymbol{B}(-\boldsymbol{q})\cdot\boldsymbol{\sigma})\hat{\Pi}^{(\nu)}(\boldsymbol{p})(\boldsymbol{v}(\boldsymbol{p})\cdot\boldsymbol{q}')\big]. \tag{A.3}$$

It is not difficult to verify that for any well behaved function $F(|\boldsymbol{p}|,|\boldsymbol{p}\times\boldsymbol{c}|)$, the following relation is valid:

$$\int\mathrm{d}^3p\ F(|\boldsymbol{p}|,|\boldsymbol{p}\times\boldsymbol{c}|)\,\mathrm{Tr}\Big[\hat{\Pi}^{(\mu)}(\boldsymbol{p})(\boldsymbol{B}(-\boldsymbol{q})\cdot\boldsymbol{\sigma})\hat{\Pi}^{(\nu)}(\boldsymbol{p})(\boldsymbol{v}(\boldsymbol{p})\cdot\boldsymbol{q}')\Big] =\tfrac{1}{2}\boldsymbol{B}(-\boldsymbol{q})\cdot(\boldsymbol{q}'\times\boldsymbol{c})\int\mathrm{d}^3p\ F(|\boldsymbol{p}|,|\boldsymbol{p}\times\boldsymbol{c}|)Q_{(\mu\nu)}(|\boldsymbol{p}|,|\boldsymbol{p}\times\boldsymbol{c}|) \tag{A.4}$$

where

$$Q_{(\mu\nu)}=\begin{pmatrix}(p/m)\sin\phi+\alpha & \alpha\\ \alpha & -(p/m)\sin\phi+\alpha\end{pmatrix}_{\mu\nu}. \tag{A.5}$$

Therefore, (A.3) can be rewritten in the form

$$T\sum_{\epsilon}\int\frac{\mathrm{d}^3q}{(2\pi)^3}\tfrac{1}{4}\mu_B\boldsymbol{B}(-\boldsymbol{q})\cdot(\boldsymbol{J}_0(\boldsymbol{q})\times\boldsymbol{c})\sum_{\mu,\nu=+,-}\int\frac{\mathrm{d}^3p}{(2\pi)^3}\frac{Q_{(\mu\nu)}}{[(\mathrm{i}\epsilon)^2-(\xi_{(\mu)})^2][(\mathrm{i}\epsilon)^2-(\xi_{(\mu)})^2]}. \tag{A.6}$$

Let us consider now the integral over ξ ($\xi=p^2/2m-\mu$) at the fixed angle ϕ:

$$I=\int\frac{\mathrm{d}\xi}{2\pi}\left(\frac{mp}{\pi}\right)\sum_{\mu,\nu=+,-}\frac{Q_{(\mu\nu)}}{[(\mathrm{i}\epsilon)^2-\xi^2_{(\mu)}(\phi)][(\mathrm{i}\epsilon)^2-\xi^2_{(\mu)}(\phi)]} \tag{A.7}$$

where $\xi_{(\pm)}(\phi) = \xi \pm \alpha p(\xi) \sin\phi$. The diagonal elements of $\hat{Q}$ contribute

$$\left(\frac{mp_F}{\pi}\right) 2\alpha(1 - 3\sin^2\phi) \frac{1}{4|\epsilon|^3} \tag{A.8}$$

to I whereas the nondiagonal elements give

$$\left(\frac{mp_F}{\pi}\right) \frac{2\alpha}{4|\epsilon|^3} \left[1 - \frac{(\alpha p_F/\pi T_c)^2 \sin^2\phi}{(|\epsilon|/\pi T_c)^2 + (\alpha p_F/\pi T_c)^2 \sin^2\phi}\right]. \tag{A.9}$$

Then, equation (A.3) takes the form

$$-\left(\frac{mp_F}{\pi}\right) \frac{1}{4\pi^3 T_c^2} \alpha\mu_B \int \mathrm{d}^3 r \; \boldsymbol{B}(\boldsymbol{r}) \cdot (\boldsymbol{J}_0(\boldsymbol{r}) \times \boldsymbol{c}) \int_0^\pi \frac{1}{2} \sin\phi \sum_{n\geq 0} \times \frac{x^2 \sin^2\phi}{(2n+1)^3[(2n+1)^2 + x^2\sin^2\phi]} \tag{A.10}$$

with $x = \alpha p_F/\pi T_c$, or, what amounts to the same,

$$-D(0)\eta \frac{3\alpha}{4 v_F p_F} f_3\left(\frac{\alpha p_F}{\pi T_c}\right) \mu_B \int \mathrm{d}^3 r \; (\boldsymbol{c} \times \boldsymbol{B}(\boldsymbol{r})) \cdot \boldsymbol{J}_0(\boldsymbol{r}). \tag{A.11}$$

Here η is as defined below equation (1.3), $D(0)$ as below (3.1), and $f_3(x)$ as is defined by equation (1.5).

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