DIAMAGNETISM OF SYSTEMS WITH ELECTRON-HOLE PAIRING

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We consider the diamagnetic properties of an isotropic model of a semimetal with electron-hole pairing. We obtain a number of general relations for the Green's function, describing such a system in a magnetic field. It is shown that the diamagnetic susceptibility of the semiconducting state differs from the Landau diamagnetic susceptibility for the semimetallic state by a small amount which vanishes at the phase-transition point.

1. Keldysh and Kopaev[1,2] have shown that in the model of a semimetal with sufficiently isotropic spectrum, at small differences between the concentrations of the electrons and holes belonging to different overlapping bands, an instability arises against the production of electron-hole pairs.

The new coherent state into which the electron system of the semimetal goes over has a number of properties which, on the one hand, are analogous to the properties of superconductors (for example, the dependence of the energy gap on the temperature), and on the other hand they are analogous to the properties of semiconductors (the dependence of the carrier density on the temperature). Jerome, Rice, and Kohn[3] introduced for such a state the term "exciton insulator" and have shown that in this state there is no strong diamagnetism or Mossbauer effect.

2. We consider a system characterized, in the absence of pairing, by two overlapping bands. We shall further take into account the Coulomb interaction between the electrons of the different bands, which on going in the valence band to the hole representation corresponds to Coulomb attraction of the electrons and holes and, as shown in[1], is "dangerous" in the sense of occurrence of instability of the chosen ground state. The Hamiltonian of such a system, in the presence of an external field, described by a vector potential $\mathbf{A}(\mathbf{r})$, has the following form (we use the units $\hbar = c = k = 1$ throughout)

$$\mathcal{H} = \int \psi_1^+(\mathbf{r})\varepsilon_1\left(\frac{\nabla}{i} - e\mathbf{A}\right)\psi_1(\mathbf{r})\,d\mathbf{r} + \int \psi_2^+(\mathbf{r})\varepsilon_2\left(\frac{\nabla}{i} - e\mathbf{A}\right)\psi_2(\mathbf{r})\,d\mathbf{r} + \int\int \psi_1^+(\mathbf{r})\psi_2^+(\mathbf{r}_1)V(\mathbf{r}-\mathbf{r}_1)\psi_2(\mathbf{r}_1)\psi_1(\mathbf{r})\,d\mathbf{r}\,d\mathbf{r}_1, \tag{1}$$

where $V(\mathbf{r})$ is the operator of the screen Coulomb interaction, the operators $\epsilon_\alpha(\mathbf{k})$ determine the single-electron spectrum in the absence of pairing in the bands $\alpha = 1$ and $\alpha = 2$, respectively. The energy is reckoned from the Fermi level.

We shall need subsequently the single-particle temperature Green's functions, which are functionals of the vector potential $\mathbf{A}(\mathbf{r})$[4]:

$$G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; iw) = -\frac{1}{2}\int_{-1/T}^{1/T} \langle \hat{T}\psi_\alpha(\mathbf{r}, \tau)\bar{\psi}_\beta(\mathbf{r}', 0)\rangle e^{i\omega\tau}d\tau, \tag{2}$$

where

$$\omega = (2n+1)\pi T, \quad n = 0, \pm1, \pm2, \ldots,$$
$$\psi_\alpha(\mathbf{r}, \tau) = e^{\tau\mathcal{H}}\psi_\alpha(\mathbf{r})e^{-\tau\mathcal{H}},$$
$$\bar{\psi}_\alpha(\mathbf{r}, \tau) = e^{\tau\mathcal{H}}\psi_\alpha^+(\mathbf{r})e^{-\tau\mathcal{H}}. \tag{3}$$

Here ψ_α—electron operators corresponding to band α, $\hat{T}$—operator of ordering in τ, and the averaging is carried out over the Gibbs canonical ensemble with Hamiltonian $\mathcal{H}$.

For the function $G_{\alpha\beta}(\mathbf{r}, \mathbf{r}', i\omega)$ we can establish a number of general properties. Using the definition (2) and the hermiticity of the operators $\mathcal{H}$, and recognizing that the reciprocal operator $\hat{T}^{-1} = \hat{T}^*$ performs ordering in the opposite direction in τ, we can easily show that the following reciprocity relation holds:

$$G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; i\omega) = G^*_{\beta\alpha}(\mathbf{r}', \mathbf{r}; i\omega). \tag{4}$$

Inasmuch as in the coordinate representation $\mathcal{H}^*(\mathbf{A}) = \mathcal{H}(-\mathbf{A})$, we get one more general relation:

$$G^*_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; i\omega|\mathbf{A}) = G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; -i\omega|-\mathbf{A}). \tag{5}$$

Following[1,4], we write the system of equations for the determination of the function $G_{\alpha\beta}(\mathbf{r}, \mathbf{r}', i\omega)$

$$(i\omega - \varepsilon_1)G_{11}(\mathbf{r}, \mathbf{r}'; i\omega) + \int V(\mathbf{r}-\mathbf{r}_1)\mathcal{Y}_{12}(\mathbf{r}, \mathbf{r}_1)G_{21}(\mathbf{r}_1, \mathbf{r}'; i\omega)\,d\mathbf{r}_1 = \delta(\mathbf{r}-\mathbf{r}'),$$
$$(i\omega - \varepsilon_2)G_{21}(\mathbf{r}, \mathbf{r}'; i\omega) + \int V(\mathbf{r}-\mathbf{r}_1)\mathcal{Y}_{21}(\mathbf{r}, \mathbf{r}_1)G_{11}(\mathbf{r}_1, \mathbf{r}'; i\omega)\,d\mathbf{r}_1 = 0. \tag{6}$$

Here, according to (4) and (5),

$$\mathcal{Y}_{12}(\mathbf{r}, \mathbf{r}'|\mathbf{A}) = \mathcal{Y}_{21}^*(\mathbf{r}', \mathbf{r}|\mathbf{A}) = \mathcal{Y}_{21}(\mathbf{r}', \mathbf{r}|-\mathbf{A}) = T\lim_{\tau\to0^-}\sum_\omega G_{12}(\mathbf{r}, \mathbf{r}'; i\omega|\mathbf{A}). \tag{7}$$

With the aid of (6) we can readily establish one more property for the case when the single-particle spectrum has a symmetry of the form $\epsilon_1 = -\epsilon_2$ (this corresponds, in particular, to equal effective masses and concentrations of the electrons and holes):

$$G_{11}(\mathbf{r}, \mathbf{r}'; i\omega) = -G_{22}(\mathbf{r}, \mathbf{r}'; -i\omega), \quad G_{12}(\mathbf{r}, \mathbf{r}'; i\omega) = G_{21}(\mathbf{r}, \mathbf{r}', -i\omega). \tag{8}$$

3. We now proceed to consider the response of the system to an external magnetic field. We consider the case of a quadratic isotropic dispersion law, when

$$\varepsilon_{1,2}(\mathbf{k}) = \pm\frac{k^2 - k_{10,20}^2}{2m_{1,2}} + \Delta\mu(T), \tag{9}$$

and k_{10} and k_{20} are the Fermi limiting momenta of the free electrons and holes at $T = 0$. $\Delta\mu(T)$ is a temperature dependent renormalization of the Fermi level, determined by the difference between the electron and hole concentrations. The current density and the electron-number density in the first band can be written in the form

$$j_1(\mathbf{r}) = \lim_{\mathbf{r}'\to\mathbf{r},\, \tau\to 0^-} \frac{e}{2m_1} T \sum_\omega e^{-i\omega\tau}\left(\frac{\nabla_\mathbf{r}}{i} - \frac{\nabla_{\mathbf{r}'}}{i} - 2e\mathbf{A}(\mathbf{r})\right) G_{11}(\mathbf{r}, \mathbf{r}'; i\omega),$$

$$N_1 = \lim_{\mathbf{r}'\to\mathbf{r},\, \tau\to 0^-} T \sum_\omega G_{11}(\mathbf{r}, \mathbf{r}'; i\omega), \qquad (10)$$

where T is the temperature, $\omega = (2n + 1)\pi T$, $n = 0, \pm 1, \pm 2, \ldots$

The expressions for the corresponding quantities in the second band are obtained by making the substitutions $1 \to 2$ and $\tau \to -\tau$.

It follows from properties (4) and (5) that the real vector j_1 is an odd functional of $\mathbf{A}$. For the case $\epsilon_1 = -\epsilon_2$ it follows in addition, from (8) and (10), that $j_1 = j_2$.

Expression (10), together with the system (6), makes it possible to consider, in principle, arbitrary temperatures and arbitrary magnetic fields. In practice, however, this is difficult to realize. We therefore confine ourselves below to consideration of the linear response to a magnetic field. In this case

$$G_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; i\omega|\mathbf{A}) = G^{(0)}_{\alpha\beta}(\mathbf{r} - \mathbf{r}'; i\omega) + G^{(1)}_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; i\omega|\mathbf{A}), \qquad (11)$$

where $G^{(1)}_{\alpha\beta}(\mathbf{r}, \mathbf{r}'; i\omega)$ is a correction that is linear in the external field, and $G^{(0)}_{\alpha\beta}(\mathbf{r} - \mathbf{r}'; i\omega)$ satisfies a system of equations of the Gor'kov type (6) with $\mathbf{A} = 0$, and is of the form

$$G^{(0)}_{\alpha\beta}(\mathbf{r} - \mathbf{r}'; i\omega) = \int e^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')} G_{\alpha\beta}(\mathbf{k}; i\omega) \frac{d\mathbf{k}}{(2\pi)^3}, \qquad (12)$$

$$G_{11}(\mathbf{k}; i\omega) = -G_{22}^*(\mathbf{k}; i\omega) = \frac{i\omega - \varepsilon_2(\mathbf{k})}{(i\omega - \varepsilon_1(\mathbf{k}))(i\omega - \varepsilon_2(\mathbf{k})) - |\Delta(\mathbf{k})|^2},$$
$$G_{12}(\mathbf{k}; i\omega) = G_{21}^*(\mathbf{k}; i\omega) = -\frac{\Delta(\mathbf{k})}{(i\omega - \varepsilon_1(\mathbf{k}))(i\omega - \varepsilon_2(\mathbf{k})) - |\Delta(\mathbf{k})|^2}. \qquad (13)$$

The function $\Delta(\mathbf{k})$, which determines the gap produced by the pairing effect in the single-particle energy spectrum, is obtained in the absence of an external field from the integral equation

$$\Delta(\mathbf{k}) = T \sum_\omega \int V(\mathbf{k} - \mathbf{k}') G_{12}(\mathbf{k}'; i\omega) \frac{d\mathbf{k}'}{(2\pi)^3}. \qquad (14)$$

An investigation of this equation can be found in[1-5]. We shall calculate the diamagnetic current for $T = 0$ and $V(\mathbf{r}) = V_0\delta(\mathbf{r})$[1]. In this case $\Delta = \text{const}$, and the field-dependent part $\Delta^{(1)}(\mathbf{k}, \mathbf{q}) = \Delta^{(1)}(\mathbf{q})$ should be proportional in the linear approximation to $(\mathbf{qA}(\mathbf{q}))$. Therefore, choosing a gauge in the form $\operatorname{div} \mathbf{A} = 0$, we get $\Delta^{(1)}(\mathbf{q}) = 0$. The transition to $T = 0$ is effected by making the substitution

$$i\omega \to \omega \pm i\delta \operatorname{sign}(\omega),$$
$$\lim_{\tau\to 0^-} T \sum_\omega e^{\mp i\omega\tau} \ldots \to \frac{1}{2\pi i} \int \ldots d\omega.$$

Using the function $G^{(1)}_{11}(\mathbf{r}, \mathbf{r}'; i\omega)$, obtained from the system (6) linearized in the field, we obtain for the Fourier component of the diamagnetic current-density

$$j_1(\mathbf{q}) = -\frac{e^2}{m_1}\frac{1}{2\pi i} \int \mathbf{k}(\mathbf{kA}(\mathbf{q})) \left\{\frac{1}{m_1} G_{11}\left(\mathbf{k} + \frac{\mathbf{q}}{2}, \omega\right) G_{11}\left(\mathbf{k} - \frac{\mathbf{q}}{2}, \omega\right) - \frac{1}{m_2} G_{12}\left(\mathbf{k} + \frac{\mathbf{q}}{2}, \omega\right) G_{21}\left(\mathbf{k} - \frac{\mathbf{q}}{2}, \omega\right)\right\} d\omega \frac{d\mathbf{k}}{(2\pi)^3} - \frac{e^2 N_1}{m_1}\mathbf{A}(\mathbf{q}), \qquad (15)$$

where

$$N_1 = \frac{1}{(2\pi i)} \int G_{11}(\mathbf{k}, \omega) \frac{d\mathbf{k}}{(2\pi)^3} d\omega. \qquad (16)$$

According to (13), the poles of the integrand of (15) are at the points $\omega = \epsilon^{(1)}, \epsilon^{(2)}$, which determine the new single-particle spectrum:

$$\varepsilon^{(1),(2)} = \delta\xi \pm \sqrt{\xi^2 + \Delta^2} + \Delta\mu', \qquad (17)$$

where

$$\xi = \frac{\varepsilon_1 - \varepsilon_2}{2} = \frac{k^2 - k_0^2}{4\mu}, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad \delta = \frac{m_2 - m_1}{m_1 + m_2},$$
$$\frac{k_0^2}{\mu} = \frac{k_{10}^2}{m_1} + \frac{k_{20}^2}{m_2}, \quad \Delta\mu' = \Delta\mu + \frac{k_{20}^2 - k_{10}^2}{2(m_1 + m_2)}.$$

Assume further that $\Delta\mu' > 0$. Then $\epsilon^{(1)}(\xi) > 0$ and the range of variation of ξ where the integrals (24) differ from zero (the poles lie on opposite sides of the integration counter) is determined from the condition $\xi^{(2)}(\xi) < 0$.

Calculating the residue at the pole $\omega = \epsilon^{(2)}$, we get

$$j_1(\mathbf{q}) = -\frac{e^2}{m_1} \int \mathbf{k}(\mathbf{kA}(\mathbf{q}))(A_+ + A_-) f(\varepsilon^{(2)}) \frac{d\mathbf{k}}{(2\pi)^3} - \frac{e^2 N_1}{m_1}\mathbf{A}(\mathbf{q}), \qquad (18)$$

$$N_1 = \int \frac{1}{2}\left(1 - \frac{\xi}{\sqrt{\xi^2 + \Delta^2}}\right) f(\varepsilon^{(2)}) \frac{d\mathbf{k}}{(2\pi)^3}, \qquad (19)$$

where

$$A_\pm = \mp \frac{\frac{1}{m_1}(\xi_\pm - \sqrt{\xi_\pm^2 + \Delta^2})\left(\pm(\delta - 1)\frac{(\mathbf{kq})}{2\mu} + \xi_\pm - \sqrt{\xi_\pm^2 + \Delta^2}\right) - \frac{1}{m_2}\Delta^2}{2\sqrt{\xi_\pm^2 + \Delta^2}\,\frac{(\mathbf{kq})}{2\mu}\left[\pm(\delta^2 - 1)\frac{(\mathbf{kq})}{2\mu} - 2\delta\sqrt{\xi_\pm^2 + \Delta^2} + 2\xi_\pm\right]},$$

$$f(\varepsilon) = \begin{cases} 0, & \varepsilon > 0 \\ 1, & \varepsilon < 0 \end{cases}; \quad \xi_\pm = \xi \pm \frac{(\mathbf{kq})}{4\mu} + \frac{q^2}{16\mu}. \qquad (20)$$

The corresponding current density for the second hole band is obtained by making the substitution $1 \to 2$, and the density of the number of holes turns out to be

$$N_2 = \int \left[1 - \frac{1}{2}\left(1 + \frac{\xi}{\sqrt{\xi^2 + \Delta^2}}\right) f(\varepsilon^{(2)})\right] \frac{d\mathbf{k}}{(2\pi)^3}. \qquad (21)$$

After simple transformations of the integrand, we obtain for the current density

$$j_1(\mathbf{q}) = -\frac{2e^2}{m_1} \int \frac{\mathbf{k}(\mathbf{kA}(\mathbf{q}))}{(\mathbf{kq} - q^2/2)} \left(1 - \frac{\xi}{\sqrt{\xi^2 + \Delta^2}}\right) f(\varepsilon^{(2)}(\xi)) \frac{d\mathbf{k}}{(2\pi)^3} - \frac{e^2 N_1}{m}\mathbf{A}(\mathbf{q}). \qquad (22)$$

Integrating with respect to the angles, we can readily get

$$j_1(\mathbf{q}) = -\frac{e^2 \mathbf{A}(\mathbf{q})}{8\pi^2 m_1} \int_0^\infty \left(k^2 - \frac{k(k^2 - q^2/4)}{q} \ln\left|\frac{k + q/2}{k - q/2}\right|\right) \times \left(1 - \frac{\xi}{\sqrt{\xi^2 + \Delta^2}}\right) f(\varepsilon^{(2)}) dk - \frac{e^2 N_1}{m_1}\mathbf{A}(\mathbf{q}). \qquad (23)$$

In the limit as $q \to 0$, the Fourier component of the current density tends to zero like $j_1(\mathbf{q}) = \chi_1 q^2 \mathbf{A}(\mathbf{q})$, i.e., there is neither strong diamagnetism nor a Mossbauer effect at any ratio of the masses and concentrations of the electrons and holes. The coefficient

[1]More accurately, the characteristic interaction radius should lie in the range [4]; $k_0^{-1} \ll r_D \ll k_0/\Delta$.

$$\chi_1 = -\frac{e^2}{24\pi^2 m_1}\int_0^\infty \left(1 - \frac{\xi}{\sqrt{\xi^2+\Delta^2}}\right) f(\varepsilon^{(2)})\, dk \tag{24}$$

is the diamagnetic susceptibility.

In the absence of pairing ($\Delta = 0$) we have

$$\chi = \chi_1 + \chi_2 = -\frac{e^2}{12\pi^2}\left(\frac{k_{10}}{m_1} + \frac{k_{20}}{m_2}\right), \tag{25}$$

i.e., the diamagnetic susceptibility of the semimetallic state coincides with the sum of the diamagnetic Landau susceptibilities for free gases of electrons and holes with the corresponding limiting Fermi momenta k_{10} and k_{20}.

At equal concentrations of the electrons and holes we get for the determination of $\Delta\mu'$, in accordance with (19) and (21),

$$N_1 - N_2 = \int (1 - f(\varepsilon^{(2)}))\frac{d\mathbf{k}}{(2\pi)^3} = 0. \tag{26}$$

Thus, the Fermi level lies in this case between the allowed bands and $\epsilon^{(2)}(\xi) < 0$ for all values

$$-k_0^2/4\mu < \xi < 0.$$

In this case we obtain after integrating by parts in (24)

$$\chi_1 = -\frac{e^2 k_0}{24\pi^2 m_1}\int_{-k_0^2/4\mu\Delta}^{\infty} \frac{(1 + (4\mu\Delta/k_0^2)x)^{1/2}\, dx}{(1+x^2)^{3/2}}. \tag{27}$$

The small parameter in the theory (see[1,4]) is the ratio $4\mu\Delta/k_0^2$, and therefore, accurate to terms of order $(4\mu\Delta/k_0^2)^2$ we have

$$\chi_1 = -\frac{e^2 k_0}{12\pi m_1}\left(1 + \frac{1}{8}\left(\frac{4\mu\Delta}{k_0^2}\right)^2 \ln\frac{4\mu\Delta}{k_0^2} + \ldots\right). \tag{28}$$

The transition from the semimetallic state to the semiconducting state is accompanied by a small decrease in the diamagnetic susceptibility.

4. From the point of view of the realignment of the single-particle spectrum, the phase transition from a semimetallic state to a semiconducting state as a result of electron-hole pairing is analogous to the phase transition from the metallic state to the superconducting state as a result of Cooper pairing. However, in external fields the behavior of the two systems is qualitatively different. Our system behaves in many respects like an ordinary semiconductor. In particular, as shown in[3], there is no Mossbauer effect in such a system, and the static electric conductivity increases with temperature in proportion to the growth of the effective number of carriers in the conduction band.

It is known[6] that in semiconductors with narrow allowed bands the quasi-coupled electrons of a completely filled valence band make a contribution comparable with the contribution from the atomic electrons to the diamagnetic susceptibility. In the present paper we consider a model for the opposite limiting case, namely a semiconductor with a narrow forbidden band. The calculations show that the diamagnetic susceptibility of the semiconducting state is determined by an expression analogous to the expression for free particles, the only difference being that the spectrum of the free particles and the distribution function are replaced by the spectrum of the single-particle excitations and the distribution function in the presence of pairing. For example, for the first band we have

$$f(\varepsilon^{(1)}) \to {}^1/_2(1 - \xi/\sqrt{\xi^2+\Delta^2}) f(\varepsilon^{(2)}).$$

It turns out that for $4\mu\Delta/k_0^2 \ll 1$ in the semiconducting phase it differs from the Landau susceptibility of the free carriers in the semimetallic state at $T = 0$ and equal electron and hole concentrations by an amount

$$\Delta\chi_1 = -\frac{e^2 k_0}{6\pi^2\mu}\left(\frac{\mu\Delta}{k_0^2}\right)^2 \ln\frac{4\mu\Delta}{k_0^2} > 0.$$

In the case of different electron and hole concentrations and at finite temperatures, this difference will be smaller, owing to the decrease in the region of integration in the integral (27) and to the decrease of Δ.

We note that the susceptibility in the semiconducting phase is determined not by the total number of valence electrons, but only by their concentration in the semimetallic phase, connected with the degree of band overlap, as expressed by the factor $f(\epsilon^{(2)})$ in (26). At sufficiently small effective masses and a large degree of overlap, the diamagnetism of the atomic electrons may become insignificant.

We have disregarded completely the dependence of the spin variables. According to[5], at a negative sign of the exchange integral, electron-hole pairing in the singlet state is energetically favored. No magnetic structure arises in this case in the system, and at $T = 0$, owing to the complete filling of the lower band, the spin paramagnetism turns out to be equal to zero. With increasing temperature, Δ decreases, the number of unpaired electrons increases, meaning that the paramagnetic susceptibility increases and can exceed under certain conditions the diamagnetic susceptibility, which depends little on the temperature. The resultant susceptibility passes through zero with change in temperature.

The fact that the diamagnetic susceptibility of the semiconducting phase turns out to be close to the Landau diamagnetic susceptibility for free electrons, suggests the possibility of quantum oscillations of the de Haas—van Alphen type. This apparently takes place in the case of different electron and hole concentrations, when the Fermi level falls in the allowed band. At equal concentrations, the Fermi level is in the forbidden band and there should be no quantum oscillations.

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