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Diamagnetism of layered organic conductors

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Temperature dependence of the magnetic susceptibility of layered organic conductors with an arbitrary dispersion law, placed in a strong magnetic field, is analyzed. It is shown that quasi-two-dimensional character of the electron energy spectrum of such conductors results in strong dependence of the diamagnetic contribution to the magnetization upon the applied magnetic field orientation. Experimental investigation of the anisotropy of the magnetic susceptibility makes it possible to study separately the diamagnetic and paramagnetic contributions to the magnetization of layered conductors.

PACS: **75.20.–g** Diamagnetism, paramagnetism and superparamagnetism.

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Spin splitting of charge carriers energy levels in a magnetic field $\mathbf{B}$ results in the magnetization of a conductor $\mathbf{M} = \chi_p \mathbf{B}$, directed along the magnetic field vector. According to Pauli [1], the paramagnetic susceptibility is proportional to the density of states of conduction electrons $\nu(\mu)$ with the energy ϵ equal to the charge carriers chemical potential μ,

$$\chi_p = \nu(\mu)\beta^2 \tag{1}$$

where $\beta = e\hbar / 2mc$ is the Bohr magneton, e, m are the electron charge and mass, $\hbar$ is the Plank constant, c is the velocity of light.

The Pauli formula (1) is only valid at temperatures T exceeding significantly the separation $\hbar\omega_c$ between the conduction electrons energy levels quantized by a magnetic field. In this range of temperatures and magnetic field values allowance for the quantization of the energy of charge carriers orbital motion leads to an additional contribution into the magnetization of the sample $\mathbf{M}_D$, opposite in direction to the magnetic field (Landau diamagnetism) [2].

In a quantizing magnetic field the density of states for each fixed energy value ε has a singularity which repeats itself with $1/B$ changing. For low enough temperature, when $T \le \hbar\omega_c$, only one quantized energy level may be placed in the region of the temperature smearing of the Fermi distribution function for conduction electrons. These singularities give rise to the oscillatory dependence of the magnetization upon $1/B$, which was predicted by Landau [2] and observed independently in bismuth by de Haas and van Alphen in Leiden [3]. At such low temperatures it is already impossible to separate the diamagnetic and paramagnetic contributions to the magnetization because account of the spin splitting of the charge carriers energy levels affect essentially the amplitude of the quantum oscillations of the magnetization and their phase [4]. Observation of this oscillation effect by Shoenberg in Cambridge in the Mond laboratory in a whole series of other metals [5] proves the universality of the de Haas–van Alphen effect. At temperatures close to zero, the amplitude of the quantum oscillations of the magnetization exceeds significantly its slowly varying part. The theory of the de Haas–van Alphen effect for an arbitrary dispersion law of charge carriers in degenerated conductors, developed by Lifshitz and Kosevich [4], is used successfully up to the present time as an infallible spectroscopic method for the determination of the Fermi surface.

The oscillation amplitude decreases with increasing temperature and decays exponentially at $T \gg \hbar\omega_c$. In this temperature range at any magnetic field orientation the Pauli paramagnetic susceptibility is determined by the charge carriers density of states at the Fermi level ε_F (equal to the chemical potential at zero-temperature) up to small corrections in a magnetic field to the chemical potential μ. However the Landau diamagnetic susceptibility

$$\chi_D = \frac{\partial}{\partial B}\left(\frac{\mathbf{M}_D \mathbf{B}}{B}\right) \tag{2}$$

is anisotropic essentially in the case of anisotropic conductors.

The interest in layered conductors which possess sharply anisotropic energy spectrum of elementary excitations, is due to the Little's suggestion [6] that superconducting state at sufficiently high temperatures is possible in conducting structures with low dimensionality. The attention was focussed on quasi-one-dimensional and quasi-two-dimensional conductors of organic origin. Electron effects in organic conductors have been investigated by many authors, the results of these studies were given in a series of surveys (see, for example, [7–11]).

In layered organic conductors the charge carriers energy

$$\epsilon(\mathbf{p}) = \sum_{l=0}^{\infty}\epsilon_l(p_x, p_y)\cos\left(\frac{alp_z}{\hbar}\right) \tag{3}$$

depends weekly on the momentum projection $p_z = \mathbf{pn}/n$ on the normal $\mathbf{n}$ to the layers, so a conduction electron moves slowly across the layers with the velocity $v_z = \partial\epsilon/\partial p_z$ which is much less than the characteristic Fermi velocity v_F,

$$v_z \le \eta v_F \ll v_F. \tag{4}$$

Here a is the separation between the layers. For the sake of compactness of calculations, harmonics changing their sign when p_z is replaced by $-p_z$, are omitted in Eq. (3). According to the measurements of kinetic coefficients of layered conductors, the parameter of quasi-two-dimensionality of the electron energy spectrum η is of the order of 10^{-2}.

Closed isoenergetic surfaces in the momentum space are only near the boundary of the energy band, and all the rest of isoenergetic surfaces, including the Fermi surface, are open and may consist of topologically different elements in the form of planes and cylinders weakly corrugated along the p_z-axis. At low temperatures the Shubnikov–de Haas oscillations of the magnetoresistance of practically all organic metals were observed [12], which indicate that at least one of the Fermi surface cavities is a weakly corrugated cylinder (see, for example, collected articles [11]). The Fermi surface of the organic conductor based on the tetrathiafulvalene $(\mathrm{BEDT-TTF})_2\mathrm{X}$ where $\mathrm{X} = \mathrm{JBr}_2, \mathrm{J}_3$, consists only of a single weakly corrugated cylinder.

We consider the diamagnetic contribution to the magnetization of charge carriers in quasi-two-dimensional conductors placed in a strong magnetic field $\mathbf{B} = (0, B\sin\theta, B\cos\theta)$.

In order to determine the magnetic susceptibility of a conductor

$$\chi = -\frac{\partial^2\Omega}{\partial B^2} \tag{5}$$

it suffices to calculate the thermodynamic potential

$$\Omega = -T\frac{eB}{c(2\pi\hbar)^2}\sum_{\pm}\sum_{n=0}^{\infty}\int dp_B \ln\left(1+\exp\frac{\mu^{\pm}-\epsilon_n(p_B)}{T}\right), \tag{6}$$

where $\mu^{\pm} = \mu \pm \beta B$, β is the Bohr magneton.

It easy to make sure that non-oscillating with the magnetic field part of the Landau diamagnetic susceptibility

$$\chi_L = -\frac{e^2}{12c^2(2\pi)^2\hbar}\sum_{\pm}\int\frac{dp_B}{m^*}\frac{1}{1+\exp\dfrac{-\mu^{\pm}+\epsilon_c(p_B)}{T}} \tag{7}$$

is formed by electrons from small vicinities of the reference points of the isoenergetic surfaces along the magnetic field direction, averaging over the conduction band, i.e. over all values of $p_B = \mathbf{pB}/B$, at which the area

$$S(\epsilon, p_B) = 2\pi\hbar\frac{eB}{c}\left(n+\frac{1}{2}\right) \tag{8}$$

of the isoenergetic surface cross-section cut by the plane $p_B = \mathrm{const}$, attains its minimum value and is close to zero. In the small vicinity $\Delta\mathbf{p} = \mathbf{p} - \mathbf{p}_0$ of the reference points $\mathbf{p}_0$ the energy at a given p_B value depends quadratically upon the momentum projection on the plane orthogonal to the magnetic field. The cyclotron effective mass in Eq. (7) $m^* = m^*(p_B) = (m_1 m_2)^{1/2}$ is expressed to a high accuracy in terms of the principal values m_1^{-1}, m_2^{-1} of the inverse effective mass tensor in the vicinity of the reference point of the isoenergetic surface.

In a magnetic field applied orthogonal to the layers plane, there are no reference points along the magnetic field direction on the open isoenergetic surfaces, and the energy values $\epsilon_c(p_B)$ for which $S(\epsilon_c(p_B), p_B) = \pi\hbar eB/c$, are placed near the boundaries of the energy band and differ essentially from the Fermi level.

When the magnetic field is deflected from the normal to the layers by the angle θ, the reference points along the **B**-vector appear on the open isoenergetic surfaces as well. The range of possible ϵ_c values at which the area of closed electron orbits is close to zero, increases with increasing θ, and at $\eta\tan\theta \gg 1$ the reference points occur on all isoenergetic surfaces.

At $\eta\tan\theta \ll 1$ the limit value of ε_c at which the reference points are already absent on the open isoenergetic surfaces, is also differs essentially from the Fermi level. This is the case when the magnitude χ_L is practically constant and temperature-dependent corrections to it are exponentially small at $T \ll \mu$. In the vicinity of the reference point the cyclotron effective mass increases in inverse proportion to $\cos\theta$ with θ increasing. As a result, the diamagnetic susceptibility decreases with the magnetic field inclination. At $\eta\tan\theta \ll 1$ the temperature dependent corrections to χ_L decrease exponentially with the temperature until $\eta\tan\theta$ attains values of the order of unity.

To clarify the above we consider the case of the simple charge carriers dispersion law

$$\epsilon(\mathbf{p}) = \frac{p_x^2 + p_x^2}{2m} - t_{\perp}\cos\left(\frac{ap_z}{\hbar}\right), \tag{9}$$

where overlap integral of the wave functions of electrons belonging to neighboring layers $t_{\perp}$ is assumed to be a constant quantity.

When $\hbar\omega_c \ll T \ll \mu$, in a magnetic field orthogonal to the layers plane the temperature dependence of the diamagnetic susceptibility of the conductor is of the form

$$\chi_L(T) = -\frac{e^2}{24\pi c^2 am}\left[1 + \sum_{N=1}^{\infty}(-1)^N \exp(-N\mu^{\pm}/T) I_0(Nt_\perp/T)\right] \tag{10}$$

where $I_0(x)$ is the modified Bessel function. Taking into account its asymptotic behavior at large values of the argument, it is easily seen that the temperature dependent correction to χ_L,

$$\chi_L(T) - \chi_L(0) = \frac{e^2}{24\pi c^2 am}\exp\left(\frac{-\mu^{\pm} + t_\perp}{T}\right)\frac{\sqrt{T}}{\sqrt{2\pi t_\perp}}, \tag{11}$$

is vanishingly small and the diamagnetic susceptibility χ_L does not practically depend upon the temperature.

Closed isoenergetic surfaces are only possible for $\epsilon < t_\perp$ (energy is counted off from the bottom of the band) or for the energy values that differ from the top of the band by a magnitude less than $t_\perp$. All the rest isoenergetic surfaces are open and have no reference points in the normal magnetic field, so $t_\perp$ is the limiting value for ϵ_c in Eq. (7).

The electron velocity in the reference point of the isoenergetic surface is always directed along the magnetic field, and its projections on the plane orthogonal to the **B** vector equal to zero:

$$v_x = \frac{\partial\epsilon}{\partial p_x} = 0, \quad v_\xi = \frac{\partial\epsilon}{\partial p_\xi} = v_y\cos\theta - v_z\sin\theta = 0, \tag{12}$$

where $p_\xi = p_y\cos\theta - p_z\sin\theta$.

Within a quadratic approach in the deviation of the momentum from its value in the reference point $\mathbf{p}_0$ we obtain the following expansion for the energy near this point

$$\epsilon(\mathbf{p}) = \epsilon(\mathbf{p}_0) + \frac{\partial^2\epsilon}{\partial p_x^2}\frac{(p_x - p_{0x})^2}{2} + \frac{\partial^2\epsilon}{\partial p_\xi^2}\frac{(p_\xi - p_{0\xi})^2}{2} \tag{13}$$

where the coefficients are

$$\frac{\partial^2\epsilon}{\partial p_x^2} = \frac{1}{m}, \quad \frac{\partial^2\epsilon}{\partial p_\xi^2} = \frac{\cos^2\theta}{m} + \sin^2\theta\,\frac{a^2 t_\perp}{\hbar^2}\cos\left(\frac{ap_{0z}}{\hbar}\right). \tag{14}$$

Thus, the inverse value of the cyclotron effective mass has the form

$$\frac{1}{m^*} = \frac{1}{m}\sqrt{\cos^2\theta + \sin^2\theta\,\frac{a^2 m t_\perp}{\hbar^2}\cos\left(\frac{ap_{0z}}{\hbar}\right)}. \tag{15}$$

The expression given above describes the behavior of the effective mass in a wide range of the angles of the magnetic field inclination. In the case when $\eta\tan^2\theta \ll 1$, the second term under in the radicand may be omitted and the mass grows in inverse proportion to $\cos\theta$ with the magnetic field inclination. If $\eta\tan^2\theta \simeq 1$, both terms in the radicand are of the same order of magnitude and the cyclotron effective mass is inversely proportional to the square root of the quasi-two-dimensionality parameter, $m^* \simeq m/\eta_0^{1/2}$, where $\eta_0 = a^2 m t_\perp/\hbar^2$ coincides with η up to a numerical factor of the order of unit.

When $\eta\tan^2\theta << 1$ the diamagnetic susceptibility

$$\chi_L(\theta) = -\frac{e^2}{48\pi^2\hbar mc^2}\sum_{\pm}\int_0^{2\pi\hbar\cos\theta/a} dp_B\,\frac{\left\{\cos^2\theta + \eta_0\sin^2\theta\cos\left[\frac{a}{\hbar}\left(\frac{p_B}{\cos и} - p_{0y}\tan\theta\right)\right]\right\}^{1/2}}{1 + \exp\frac{-\mu^{\pm} + \epsilon_c(p_B)}{T}} \tag{16}$$

does not practically depend on the temperature such as in the case of the the normal magnetic field. Replacing in Eq. (16) the Fermi distribution function by unit we obtain for χ_L at $\lambda < 1$ the follkowing expression

$$\chi_L(\theta) = -\frac{e^2\cos^2\theta}{24\pi^2 amc^2}\int_0^{2\pi} d\varphi\sqrt{1 + \lambda\cos\varphi} =$$

$$= -\frac{e^2\cos^2\theta}{12\pi amc^2}\left[\sqrt{1-\lambda}\,E\left(\sqrt{\frac{2\lambda}{-1+\lambda}}\right) + \sqrt{1+\lambda}\,E\left(\sqrt{\frac{2\lambda}{1+\lambda}}\right)\right], \tag{17}$$

where $\lambda = \eta_0\tan^2\theta$, $E(x)$ is the complete elliptic integral.

When $\lambda \ll 1$ the expression for χ_L takes the form

$$\chi_L(\theta) = -\frac{e^2\cos^2\theta}{12\pi amc^2}\left[1 - \left(\frac{\lambda}{4}\right)^2\right]. \tag{18}$$

At the same time the paramagnetic susceptibility depends essentially upon the temperature because the chemical potential decreases markedly with increasing T. Exclusion is the case of the quasi-two-dimensional energy spectrum for charge carriers (9). In this case for any temperature $T << \mu$ the density of states $\nu(\mu) = m/\pi\hbar^2 a$ is the constant value to within small corrections proportional to η^2. As a result the temperature dependence of the paramagnetic susceptibility appears only in quadratic approach in the small parameter of the quasi-two-dimensionality of the electron energy spectrum. In fact the charge carriers dispersion law in organic conductors differs substantially from the exotic energy spectrum (9) given above. The essentially different temperature dependences of the diamagnetic and paramagnetic susceptibility allows to study them separately.

The expression (16) for χ_L with the effective mass (15) describes to a large extend the diamagnetic susceptibility of an organic quasi-two-dimensional conductor with an arbitrary charge carriers dispersion law, because in calculating χ_L, it is sufficient that we confine ourselves to the quadratic approximation in the expansion in power series about $(p_x - p_{0x})$ and $(p_\xi - p_{0\xi})$ of the energy

$$\epsilon(\mathbf{p}) = \epsilon(\mathbf{p}_0) + \frac{1}{2}\alpha_{ij}(p_z - p_{0z})(p_j - p_{0j}),$$
$$\alpha_{ij} = \frac{\partial^2 \epsilon}{\partial p_i \partial p_j}\Big|_{\mathbf{p}=\mathbf{p}_0}. \tag{19}$$

After reducing the tensor α_{ij} to the diagonal form we obtain the expression analogous to (13) with turned axes. The area of the isoenergetic surface cross section in the form of an ellipse is independent on the axes orientation and we have

$$S(\varepsilon, p_0) = 2\pi(\varepsilon - \varepsilon(p_0))m^*, \tag{20}$$

where

$$m^* = \left\{\cos^2\theta\left[\frac{\partial^2\epsilon}{\partial p_x^2}\frac{\partial^2\epsilon}{\partial p_y^2} - \left(\frac{\partial^2\epsilon}{\partial p_x \partial p_y}\right)^2\right] + \right.$$
$$+ 2\sin\theta\cos\theta\left[\frac{\partial^2\epsilon}{\partial p_x \partial p_y}\frac{\partial^2\epsilon}{\partial p_x \partial p_z} - \frac{\partial^2\epsilon}{\partial p_x^2}\frac{\partial^2\epsilon}{\partial p_y \partial p_z}\right] +$$
$$\left. + \sin^2\theta\left[\frac{\partial^2\epsilon}{\partial p_x^2}\frac{\partial^2\epsilon}{\partial p_z^2} - \left(\frac{\partial^2\varepsilon}{\partial p_x \partial p_z}\right)^2\right]\right\}^{-1/2}. \tag{21}$$

In a two-dimensional conductor $(\eta = 0)$ charge carriers do not respond to the presence of a magnetic field in the layers plane. As appears from Eq. (15) and Eq. (21) at $\theta = \pi/2$, the diamagnetic susceptibility differs from zero only for $\eta \neq 0$ and increases proportionally to η^2 with η increasing. At the same time, when $(\pi/2 - \theta) \le \eta^{1/2}$, the paramagnetic susceptibility (remaining constant for any orientation of a magnetic field) exceeds significantly the diamagnetic susceptibility

In a wide range of the angles of the magnetic field inclination, namely when

$$1 \le \tan\theta \ll \frac{1}{\eta}, \tag{22}$$

the reference points of the isoenergetic surface are located near intersection of the lines $v_x = 0$ and $v_y = 0$. Because of the central symmetry of the charge carriers energy $\epsilon(-\mathbf{p}) = \epsilon(\mathbf{p})$, these points are situated on the whole p_z-axis at $p_x = p_y = 0$. Under the assumption that there are no other cross points of the lines $v_x = 0$ and $v_y = 0$ within the unit cell of the momentum space, the coefficient of $\cos^2\theta$ in Eq. (21) should be put equal to its value at $p_x = p_y = 0$ (up to small corrections of the order of $\eta\tan\theta$). Then, in the range of angles satisfying the condition (22), the expression for the magnetic susceptibility takes the form

$$\chi_L(\theta) = \chi_L(0)\cos^2\theta. \tag{23}$$

Thus investigation of the temperature and angular dependencies of the magnetic susceptibility of layered conductors enables one to study separately the diamagnetic and paramagnetic contributions to their magnetization.

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