

## SOME PROBLEMS OF THE ELECTRON THEORY OF METALS

## II. STATISTICAL MECHANICS AND THERMODYNAMICS OF ELECTRONS IN METALS\*

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Usp. Fiz. Nauk 78, 411-461 (November, 1962)

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## INTRODUCTION

IN the present survey we treat the properties of metals in thermodynamic equilibrium at low temperatures. Mainly we consider those phenomena and properties which are sensitive to the dispersion law of the conduction electrons.

The presentation is made mainly on the basis of the "gas model," i.e., almost everywhere it is assumed that the conduction electrons form a gas of charged quasiparticles. Aside from its simplicity, such a presentation is justified by the fact that, in most cases, results obtained from the model of a Fermi liquid<sup>[2]</sup> coincide with those found in the "gas approximation." In all cases where this is a discrepancy between the two models, this is pointed out. One should of course remember that the concept of a "conduction electron" as an elementary excitation with a definite quasimomentum and energy is meaningful only for excitations with energies of the order of the Fermi energy.<sup>[2]</sup> Strictly speaking, by an elementary excitation of the electron system of a metal one should mean the elementary excitation (with a definite quasimomentum  $p$ ) above the ground state of the metal, which is described by a Fermi step function.

In the course of our discussion we shall frequently also use the term "conduction electron" for excita-

tions whose energies are not close to the Fermi energy. But the overwhelming majority of the final results contained in this summary are determined by electrons with energies of the order of the Fermi energy, which makes these results reliable.

The authors have not tried to cover all the recent work, so the literature references do not constitute a bibliography.

During the three years since the appearance of the first part of this survey, many papers have appeared on the mechanics (classical and quantum) of electrons with a complicated dispersion law. These results are discussed in the Appendix.

## 1. FERMI ENERGY. FERMI SURFACE. NUMBER OF ELECTRONS

The study of the thermodynamics of the electron gas should start from its properties in the ground state, i.e., at absolute zero.

The band picture of the electron energy spectrum is very important for the understanding of the properties of solids in general and metals in particular: in a solid the regions of admissible values of the electron energy (the energy bands or zones) are separated by regions of forbidden values. The state of an electron in a band (which we shall number by the symbol  $s$ ) is characterized by the projection of its spin on some axis ( $\sigma = \pm 1/2$ ) and its quasimomentum  $p$ ; states differing in quasimomentum by an amount  $2\pi\hbar b$ , where  $b$  is a vector of the reciprocal lattice, are physically

\*The first part of this paper was published in UFN 69, 419 (1959), Soviet Phys. Uspekhi 2, 831 (1960).

equivalent. Consequently the electron energy depends on discrete parameters: the band number  $s$  and the spin projection  $\sigma$ , as well as a continuous vector parameter—the quasimomentum  $\mathbf{p}$ :

$$\varepsilon = \varepsilon_s^\sigma(\mathbf{p}). \quad (1.1)$$

The band character of the energy spectrum is a consequence of the periodic dependence of the energy on the quasimomentum  $\mathbf{p}$ : for fixed  $s$  and  $\sigma$ , when  $\mathbf{p}$  ranges over one period (i.e., over the region of a cell in the reciprocal space, multiplied by  $2\pi\hbar$ ), the energy runs through all values corresponding to the  $s$ -th band\*. The energy bands may overlap, but the individuality of the bands is maintained, since each band has its own dispersion law (1.1).

The presence of bands, partially filled with electrons at absolute zero, is characteristic of metals (conductors). For dielectrics (insulators) the bands are either completely filled or are empty.

Complete filling of an energy band corresponds to a uniform filling of the quasimomentum space ( $\mathbf{p}$ -space). Since no more than two electrons (with opposite spin directions) can be in each cell in phase space, it is clear that each band can contain no more than  $2\mathfrak{N}$  electrons, where  $\mathfrak{N}$  is the number of unit cells in the crystal. If energy bands never overlapped, all crystals with an even number of electrons in the unit cell would be dielectrics, and those with an odd number would be metals. The overlapping of the bands makes such a classification completely incorrect and explains the fact that most elements are metals in their ground state.

As a rule, in metals there are several partially filled bands. These are called conduction bands. They are the bands which are responsible for the "metallic" properties of metals, and in particular for electrical conductivity. The electrons which uniformly fill the  $\mathbf{p}$ -space and belong to the deeper-lying bands, practically do not participate in the thermal motion,† since to excite them (i.e., to make a transition into the conduction band) requires an energy of the order of a few eV. Thus one of the most important characteristics of a metal is the number  $N$  of electrons in partially filled bands. This number should, as we have seen, vary very little with temperature. Also the total number of electrons in unfilled bands should be equal to an integer times the number of atoms in the crystal.

The whole electron system has a single chemical potential  $\zeta$ , which at absolute zero determines the level of occupation of the energy bands by electrons (Fig. 1). Often the chemical potential is measured from the bottom of the corresponding band. Naturally

\*Here, and practically everywhere in this paper, we do not take account of the dependence of the electron energy on the spin projection  $\sigma$ , but assume that each electron state is doubly degenerate.

†More precisely, they move together with the lattice.

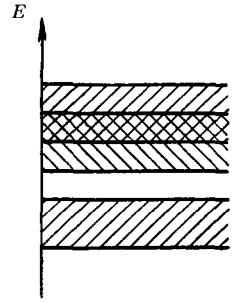


FIG. 1. Overlapping of energy bands. The shaded regions are the allowed energy values.

then each band has its own chemical potential  $\zeta_i = \zeta - \epsilon_{0i}$ , where  $\epsilon_{0i}$  is the energy corresponding to the bottom of the band. The energy below which all the electronic states are occupied at  $T = 0$  is called the limiting Fermi energy  $\epsilon_F$ , and the corresponding constant-energy surface is called the Fermi surface. For a gas of free electrons the Fermi surface is a sphere whose radius  $p_F$  is determined by the electron density:

$$p_F = 2\pi\hbar \left( \frac{3n}{8\pi} \right)^{1/3}. \quad (1.2)$$

In the case of a dielectric the limiting Fermi energy coincides with the boundary of one of the energy bands. The Fermi surface then degenerates to a point.

In a metal the limiting Fermi energy is located within one of the energy bands. The Fermi surface is a complicated periodic surface which, in most metals, runs continuously through the whole reciprocal lattice (an open surface, in the terminology of [1]).

If the Fermi surface is closed, it obviously is repeated periodically in each cell in  $\mathbf{p}$ -space. Since the electrons occupy only those parts of  $\mathbf{p}$ -space where  $\epsilon < \epsilon_F$ , the number  $n$  of conduction electrons per unit cell\* is

$$n = \frac{2}{\Delta} \Delta_F, \quad \Delta_F = \int_{(\Delta)} E(\varepsilon - \varepsilon_F) d\tau_p, \quad d\tau_p = dp_x dp_y dp_z. \quad (1.3)$$

The integration extends over the volume  $\Delta$  of the unit cell in  $\mathbf{p}$ -space, while

$$E(x) = \begin{cases} 1, & x < 0, \\ 0, & x > 0. \end{cases} \quad (1.4)$$

If the Fermi surface is closed,  $\Delta_F$  is the volume contained within the Fermi surface. We note that the surface may split into several parts, all within one unit cell.

When there are several partially filled bands in the metal, the Fermi surface breaks up into several surfaces (equal in number to the number of unfilled bands) and the nature of the overlapping of these surfaces, if they do overlap, is strictly determined by the principle that terms do not cross<sup>[4]</sup> (cf. below). The value of  $\Delta_F^S$  for each of the surfaces is determined by the number of electrons per unit cell in the corresponding band

\*Obviously the density of electrons is  $\frac{N}{V} = \frac{\Delta}{(2\pi\hbar)^3} n = \frac{2\Delta_F}{(2\pi\hbar)^3}$ .

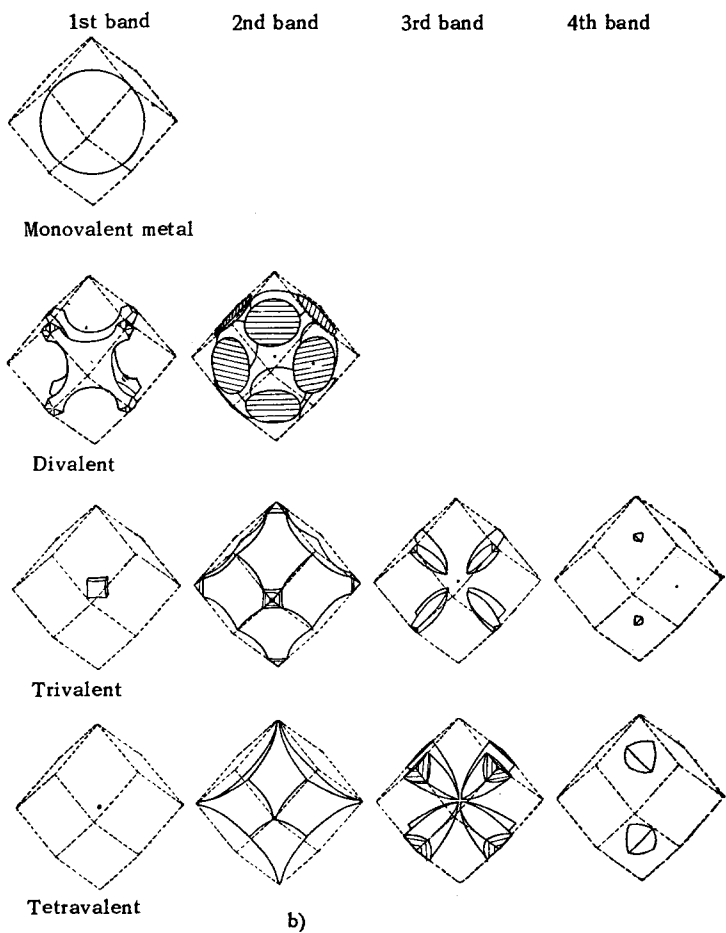
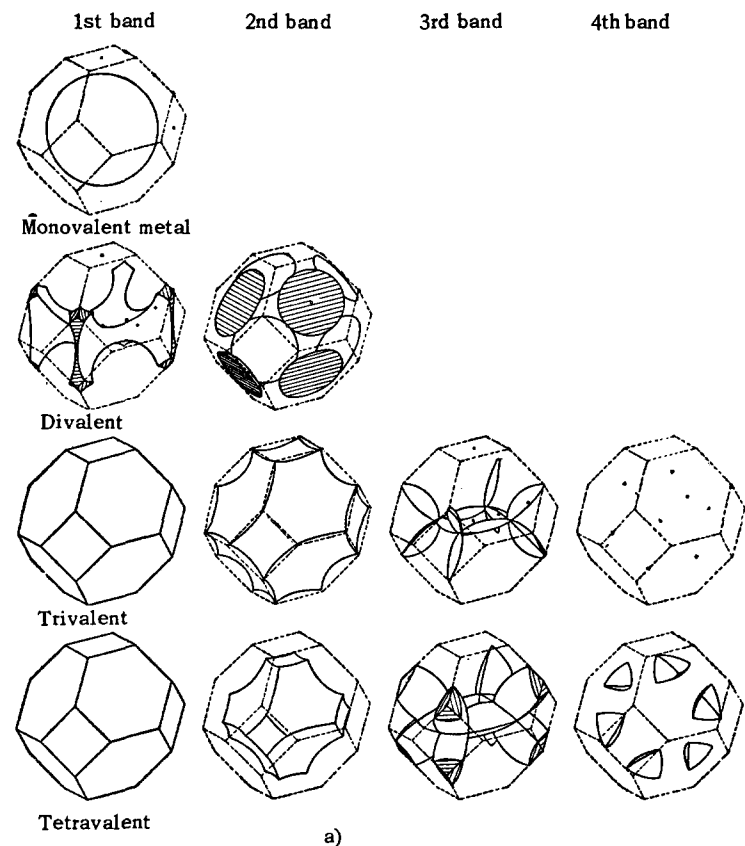


FIG. 2. Fermi surfaces for polyvalent metals: a) face-centered cubic lattice; b) body-centered cubic lattice.

$$\frac{2\Delta_F^s}{\Delta} = n_s. \tag{1.5}$$

Naturally,

$$\sum n_s = n. \tag{1.6}$$

We see immediately that  $n_s$  may depend on temperature, since an increase in temperature leads to a redistribution of electrons among the bands.

Theoretical computation of the shape of the Fermi surface for all metals is a problem which is not solvable at present. The natural procedure is therefore to determine the shape of the Fermi surface from experimental data (cf. Sec. 9). But such a problem cannot be solved without introducing trial models. In constructing such models one most often uses either the approximation of almost free electrons (Harrison et al.<sup>[5]</sup>) or the bound-electron approximation introduced by Bloch<sup>[6]</sup>. The most important point in both these models is the careful inclusion of the crystal symmetry, which makes it possible to deduce the general shape of the surface and to find the points where degeneracy must occur. One can then determine the structure of the regions of the Fermi surface which split off (cf., for example, <sup>[7]</sup>).

The idea of the first method (almost-free electrons) is that the entire anisotropy of the Fermi surface is a consequence of the crystal periodicity: in zero approximation the Fermi surface is a set of non-intersecting spherical surfaces drawn around equivalent points in the reciprocal lattice. The inclusion of the interaction amounts to the removal of the degeneracy at the points of overlap (Fig. 2). It should be mentioned that the Fermi surfaces found in this way are in many cases in fair agreement with the experimental data.

The other approximation (tight binding) uses an expansion of the energy in Fourier series, and the model aspect of the method consists in using not the entire series but only a few terms which satisfy all the symmetry requirements of the crystal. The possible types of Fermi surfaces for various metals (Ag, Au, etc) are treated in this way in a paper of Moliner<sup>[8]</sup> (cf. also <sup>[9]</sup>). The Fermi surfaces found in this way do agree with the experimental results (cf., for example, <sup>[10]</sup>) and in many cases are very similar to the surfaces obtained from the model of weakly bound electrons. The similarity of the results obtained by the different methods is explained by the fact that both methods correctly take into account the symmetry elements of the crystal.

Let us consider in more detail those cases where the Fermi surface is located near singular points in  $p$ -space. First of all we should look at the case where the Fermi surface is near the value  $p = p_0$  where the energy for the particular band has a minimum  $\epsilon(p_0) = \epsilon_0$ . The Fermi surface is then an ellipsoid with semi-axes  $\sqrt{2m_1(\epsilon_F - \epsilon_0)}$ ,  $\sqrt{2m_2(\epsilon_F - \epsilon_0)}$ ,  $\sqrt{2m_3(\epsilon_F - \epsilon_0)}$ ,

where  $m_1$ ,  $m_2$ , and  $m_3$  are the principal values of the effective mass tensor  $(\partial^2\epsilon/\partial p_i\partial p_k)_{p=0}$ . From formula (1.5) we then find

$$\epsilon_F - \epsilon_0 = \left(\frac{3N_s}{8\pi V}\right)^{2/3} \frac{(2\pi\hbar)^3}{2\sqrt[3]{m_1 m_2 m_3}}. \tag{1.7}$$

If the Fermi surface is near the value  $p = p_1$  where  $\epsilon(p)$  reaches a maximum  $\epsilon(p_1) = \epsilon_1$ , the Fermi surface is again ellipsoidal. Its semi-axes are  $\sqrt{2m'_1(\epsilon_1 - \epsilon_F)}$ ,  $\sqrt{2m'_2(\epsilon_1 - \epsilon_F)}$ ,  $\sqrt{2m'_3(\epsilon_1 - \epsilon_F)}$ , where  $m'_1$ ,  $m'_2$ , and  $m'_3$  are the negative of the principal values of the effective mass tensor. The quantity  $\epsilon_1 - \epsilon_F$  is often related to the number of free electron states in the zone,  $N'_s$ :

$$\epsilon_1 - \epsilon_F = \left(\frac{3N'_s}{8\pi V}\right)^{2/3} \frac{(2\pi\hbar)^3}{2\sqrt[3]{m'_1 m'_2 m'_3}}. \tag{1.8}$$

We have considered cases where the Fermi surface within a given band is an ellipsoid. As we have seen, this occurs when the Fermi energy  $\epsilon_F$  in the zone is close to the minimum value  $\epsilon_0$  or the maximum value  $\epsilon_1$  in the zone.

Cases can occur where only a small part of the Fermi surface is ellipsoidal. This can occur when the Fermi energy  $\epsilon_F$  is close to one of those critical values  $\epsilon_k$  at which a newly split-off sheet of the surface appears (Fig. 3). The portion of the Fermi surface near the point  $p = p_k$  where the new sheet is formed is described well by the equation of an ellipsoid. The number of electrons inside the ellipsoid (if  $\epsilon_F > \epsilon_k$ ) or the number of empty states inside the ellipsoid (if  $\epsilon_F < \epsilon_k$ ) is related to  $\epsilon_F - \epsilon_k$  by formula (1.7) in the first case and by formula (1.8) in the second.

Another class of singular points are the conical points (Fig. 4). They are located on those constant-energy surfaces which separate surfaces with different topologies (in particular they may separate open from closed surfaces, Fig. 5). We shall also regard those energy values at which a change in the topology of the constant-energy occurs as critical energies, and denote them by  $\epsilon_k$ . If the Fermi energy  $\epsilon_F$  is close to  $\epsilon_k$ ,

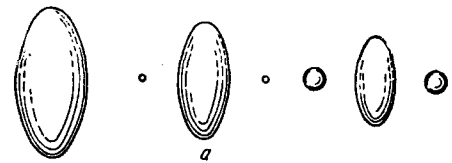


FIG. 3. Appearance of a new sheet of the constant-energy surface. Surface a corresponds to the critical energy  $\epsilon_k$ .

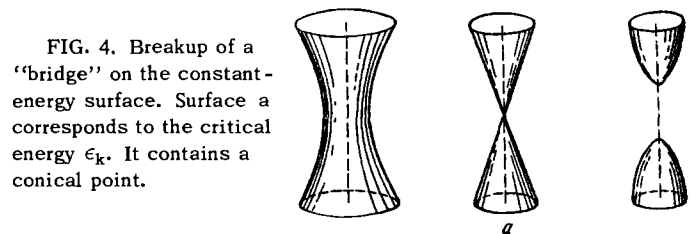


FIG. 4. Breakup of a "bridge" on the constant-energy surface. Surface a corresponds to the critical energy  $\epsilon_k$ . It contains a conical point.



different zones intersect. Thus an electron with quasi-momentum  $p'$  (Fig. 7) has energy equal to either  $\epsilon$  or  $\epsilon'$  depending on which zone it belongs to [i.e., its energy is either  $\epsilon_S(p') = \epsilon$  or  $\epsilon_{S'}(p') = \epsilon'$ ]. As both the theoretical treatment and the experimental data show, the Fermi surface of graphite is a surface of this type<sup>[12]</sup> (Fig. 8).

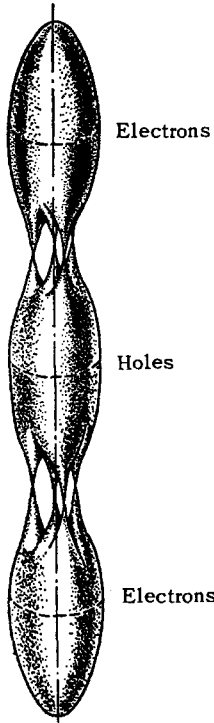


FIG. 8. General form of the Fermi surface of graphite.

We also note that formula (1.5), which relates the volume contained within the Fermi surface  $\Delta_F$  to the number of electrons in the band  $n_S$  does not require any generalization to the case of intersection of constant-energy surfaces.

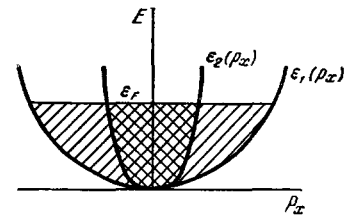
Degeneracy very often is a consequence of the crystal symmetry. It usually occurs along certain definite lines in  $p$ -space (for example, along the principal axis in the case of graphite). These values of quasimomentum are selected in such a way that usually the energy reaches its minimum (or maximum) value at these points.

If two bands have the same common minimum, then though they have the same limiting energy the numbers of electrons in the bands are not necessarily the same (Fig. 9).

Gases can occur where the minimum for one band coincides with the maximum for another band. If in such a case the lower band is completely filled while the upper band is empty, such bands should be treated as though the Fermi surface had degenerated to a point. In solids with such an electron spectrum one should observe many interesting properties similar to those of semiconductors.

For most metals the number of electrons per unit cell is close to one. Exceptions are the metals of the

FIG. 9. Filling of energy bands having a common minimum. When they are filled to the same level ( $\epsilon_1 \leq \epsilon_F$ ,  $\epsilon_2 \leq \epsilon_F$ ), the numbers of electrons in the bands are different.



fifth group of the periodic table (Sb, As, Bi) for which the number of conduction electrons per unit cell is  $\sim 10^{-5}$ . The crystal lattices of all these metals are similar. They belong to the rhombohedral system with two atoms per unit cell, and have the special feature that they are obtained from simple cubic lattices with one atom per cell by a slight displacement of the atoms. Crystals with an odd number of atoms per unit cell\* should be good metals. However, a change in the translational symmetry leading to a doubling of the volume of the unit cell markedly changes the number of electrons in the conduction band and may even in principle change the metal to a dielectric (cf. Fig. 10, in which, as an example, we consider the doubling of the period for the one- and two-dimensional cases).

If the Fermi surface passes sufficiently close to a point where there must be a degeneracy (in the  $p$ -space), A. A. Abrikosov and L. A. Fal'kovskii have shown<sup>[13]</sup> group-theoretically that under certain extremely general conditions it is favorable to form small (but finite) interior deformations in a cubic lattice, which lead to a reduction of its symmetry and a doubling of the volume of the unit cell. It seems that there is no need to look for some special physical reasons for the fact that the Fermi surface passes near to points where there must be a degeneracy (located at the boundaries of the Brillouin zone), since the surface of a sphere with a volume corresponding to the number of electrons in the unit cell passes extremely close (numerically) to the boundaries of the Brillouin zone. Since, as Harrison<sup>[5]</sup> has shown, the weak binding model gives a good approximation to the experimentally determined shapes of the Fermi surfaces for polyvalent metals, it is highly probable that the argument based on the use of the weak binding model is convincing enough.

In treating the energy structure of the ground state of the electrons in a metal, we have started from the existence of single-particle excitations of the Fermi type (conduction electrons). We know that such a treatment is justified for electrons with energies close to  $\epsilon_F$ , since the lifetime of an excitation decreases rapidly with increase of  $|p - p_F|$ , where  $p_F$  is the quasimomentum at the Fermi surface.<sup>[3]</sup> Thus expressions which contain the dispersion law for the "deep" electrons, i.e., the electrons with energy much less than  $\epsilon_F$ , are to some extent a matter of conven-

\*Remember that As, Sb, and Bi have an odd number of electrons per atom (fifth group!).

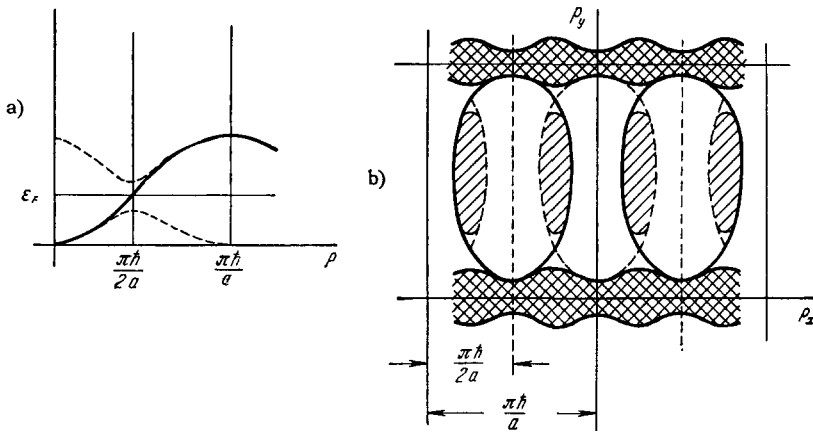


FIG. 10. Change in electron energy spectrum as a result of doubling the period. a) one-dimensional case: as a result of doubling the period, the "metal" with electrons filling half the band is changed to a dielectric; b) two-dimensional case: as a result of doubling the period along the x axis, the number of conduction electrons in the "metal" with an initially half-filled band is sharply reduced. A small electron band (shaded region) and a small hole band (cross-hatched region) have appeared.

tion. For example, formulas (1.3) and (1.4) should be regarded as the definition of the electron number density. The derivation of the total number of electrons in unfilled bands is apparently independent of the nature of the interaction between the electrons, since it is based on the indeterminacy principle and on the theorem that the number of elementary excitations of the Fermi type is equal to the number of electrons (L. Landau,<sup>[2]</sup> Luttinger<sup>[14]</sup>).

2. DENSITY OF ELECTRON STATES PER UNIT ENERGY RANGE

To develop the thermodynamics of conduction electrons, one must know the density of electron states per unit energy range,  $\nu(\epsilon)$ . This quantity is closely related to the dispersion law.

The number of states of electrons of the s-th zone in unit volume of momentum space is

$$dn_p^{(s)} = \frac{2V}{(2\pi\hbar)^3} dp_x dp_y dp_z. \tag{2.1}$$

Since the state of an electron is characterized completely by its position on the constant-energy surface  $\epsilon_s(\mathbf{p}) = \epsilon$ , while the element of volume  $dp_x dp_y dp_z$  is equal to  $ds d\epsilon/v$ , where  $ds$  is the element of area on the constant-energy surface  $\epsilon_s(\mathbf{p}) = \epsilon$ , and  $v_s = |\nabla_{\mathbf{p}} \epsilon_s(\mathbf{p})|$  is the absolute value of the electron velocity,\* by integrating (2.1) over the surface of constant energy, we find that the number of electron states  $dn_\epsilon^{(s)}$  in the energy interval  $d\epsilon$  is equal to  $(\epsilon_s(\mathbf{p}) = \epsilon)$

$$dn_\epsilon^{(s)} = \nu_s(\epsilon) d\epsilon, \tag{2.2}$$

where

$$\nu_s(\epsilon) = \frac{2V}{(2\pi\hbar)^3} \oint \frac{ds}{v_s} \tag{2.3}$$

is the density of states in the s-th zone per unit energy

\* $|\nabla_{\mathbf{p}} \epsilon_s(\mathbf{p})|^{-1}$  is the Jacobian of the transformation from the variables  $p_x, p_y, p_z$  to the variables  $\xi, \eta, \epsilon$ , where  $\xi, \eta$  are any orthogonal coordinate system on the surface  $\epsilon_s(\mathbf{p}) = \epsilon$  ( $ds = d\xi d\eta$ ).

range. Independent of whether the constant-energy surface is closed or open, the integration in (2.3) is taken over the unit cell in the reciprocal lattice; in those cases where the surface  $\epsilon_s(\mathbf{p}) = \epsilon$ , splits into several sheets,  $\nu_s(\epsilon)$  is naturally the sum of the corresponding integrals.

We note that  $\nu_s(\epsilon)$  is a unique characteristic of the electron energy spectrum, which in the "gas" approximation (omitting interaction of the electrons) is necessary for constructing a statistical thermodynamics of the conduction electron electron gas in the quasi-classical approximation.

Since  $ds d\epsilon/v$  is the volume element, (2.3) can be rewritten as follows:

$$\nu_s(\epsilon) = \frac{2V}{(2\pi\hbar)^3} \left| \frac{d\Delta_\epsilon^{(s)}}{d\epsilon} \right|, \tag{2.4}$$

where

$$\Delta_\epsilon^{(s)} = \int_{(\Delta)} E[\epsilon_s(\mathbf{p}) - \epsilon] d\tau_{\mathbf{p}}. \tag{2.5}$$

The function  $E(x)$  is defined by (1.4).

If the surface  $\epsilon_s(\mathbf{p}) = \epsilon$  is closed,  $\Delta_\epsilon^{(s)}$  is the volume contained within this surface.

The quantity  $\frac{2V}{(2\pi\hbar)^3} \Delta_\epsilon^{(s)}$  determines the number of electron states in the s-th zone with energy less than  $\epsilon$ . We denote this quantity by  $N_s(\epsilon)$ . Then

$$\nu_s(\epsilon) = \left| \frac{dN_s(\epsilon)}{d\epsilon} \right|. \tag{2.6}$$

In general the density of electron states  $\nu(\epsilon)$  is a complicated function of its argument. Its explicit form can be found only under special assumptions about the dispersion law for the conduction electrons.

In the case of a free electron gas,  $\nu(\epsilon)$  is proportional to  $\sqrt{\epsilon}$ :

$$\nu(\epsilon) = \frac{\sqrt{2}}{\pi^2} \frac{V}{\hbar^3} m^{3/2} \epsilon^{1/2}. \tag{2.7}$$

A similar dependence of the density of electron states per unit energy range occurs for energies near to the minimum or maximum values in the zone. Since

the corresponding constant-energy surfaces are ellipsoids, near a minimum ( $\epsilon \gtrsim \epsilon_0$ )

$$\nu(\epsilon) = \frac{\sqrt{2}}{\pi^2} \frac{V}{\hbar^3} \sqrt{m_1 m_2 m_3} (\epsilon - \epsilon_0)^{1/2}, \quad (2.8)$$

while near a maximum ( $\epsilon \lesssim \epsilon_1$ )

$$\nu(\epsilon) = \frac{\sqrt{2}}{\pi^2} \frac{V}{\hbar^3} \sqrt{m'_1 m'_2 m'_3} (\epsilon_1 - \epsilon)^{1/2}. \quad (2.8')$$

Thus near the extremal points ( $\epsilon = \epsilon_0$  and  $\epsilon = \epsilon_1$ ), the density of electron states has a singularity of the type  $(\epsilon - \epsilon_k)^{1/2}$ . A singularity of this type is characteristic for all those energy values at which the topology of the constant-energy surfaces changes. From this point of view, a minimum is a point at which a new sheet of the constant-energy surface appears, while a maximum is a point at which a sheet disappears. The appearance or disappearance of a sheet can also occur in the middle of the zone for certain "critical" values of the energy  $\epsilon = \epsilon_k$  (cf. Fig. 3). Then for energies close to  $\epsilon_k$ , the density of electron states  $\nu(\epsilon)$  can be represented as follows:

$$\nu(\epsilon) = \nu_0(\epsilon) + \delta\nu(\epsilon), \quad (2.9)$$

where  $\nu_0(\epsilon)$  is a smooth function of the energy, while  $\delta\nu(\epsilon)$  differs from zero on the side of the critical value where the number of sheets has increased by one. Suppose for concreteness that the number of sheets increases with increasing energy. Then

$$\delta\nu(\epsilon) = \begin{cases} 0 & (\epsilon < \epsilon_k), \\ \frac{\sqrt{2}}{\pi^2} \frac{V}{\hbar^3} \sqrt{m_1 m_2 m_3} (\epsilon - \epsilon_k)^{1/2} & (\epsilon \geq \epsilon_k). \end{cases} \quad (2.10)$$

As we stated in the preceding section, an increase in the number of sheets of the constant-energy surface can occur not only by the "birth" of new sheets (cf. Fig. 3), but also by the "breaking" of bridges\* (cf. Figs. 4-5). Let us consider this case of a change in the topology in somewhat more detail. We shall assume that the constant-energy surface  $\epsilon(\mathbf{p}) = \epsilon_k$  contains a conical singular point  $\mathbf{p} = \mathbf{p}_k$ . For energies less than  $\epsilon_k$ , the surface near the point  $\mathbf{p} = \mathbf{p}_k$  is well approximated by the equation of a hyperboloid with two sheets, and for  $\epsilon > \epsilon_k$  by the equation of a paraboloid. With a suitable choice of coordinate axes, the equation of the constant-energy surface near  $\mathbf{p} = \mathbf{p}_k$  ( $\epsilon \sim \epsilon_k$ ) is written as follows:

$$\epsilon = \epsilon_k + \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{p_3^2}{2m_3} \quad (m_1, m_2, m_3 > 0). \quad (2.11)$$

Calculating the volume bounded by the surface (2.11) and the plane  $p_3 = \text{const}$  (the  $p_3$  axis is along the axis of the bridge), we find

\*A change in the topology of the constant-energy surfaces can also occur without a change in the number of sheets (for example, breaking of a bridge on a toroidal surface). In such cases the connectivity of the surface changes at the point  $\epsilon = \epsilon_k$ , and  $\delta\nu(\epsilon) \neq 0$  in the region where the connectivity is lower.

$$\Delta(\epsilon, p_3) = \begin{cases} \frac{2\pi p_3^3}{3} \frac{\sqrt{m_1 m_2}}{m_3} + 4\pi \sqrt{m_1 m_2} (\epsilon - \epsilon_k) p_3 & (\epsilon > \epsilon_k), \\ \frac{2\pi p_3^3}{3} \frac{\sqrt{m_1 m_2}}{m_3} + 4\pi \sqrt{m_1 m_2} (\epsilon - \epsilon_k) p_3 \\ \quad + \frac{8\pi}{3} \sqrt{2m_1 m_2 m_3} (\epsilon_k - \epsilon)^{3/2} & (\epsilon < \epsilon_k). \end{cases} \quad (2.12)$$

It is clear that in this case also the density of electron states  $\nu(\epsilon) \sim d\Delta/d\epsilon$  can be written as a sum of two terms: a smooth function  $\nu_0(\epsilon)$  and an irregular term  $\delta\nu(\epsilon)$ , which has a "root" singularity and differs from zero for those energies where the number of sheets is the larger value (cf. also the last footnote).

Expression (2.10) remains valid [the significance of  $m_1, m_2$ , and  $m_3$  is evident from (2.11)].

We have considered typical singular points associated with a change in the topology of the constant-energy surfaces. It may happen that the singular point  $\mathbf{p} = \mathbf{p}_k$  is also a point of degeneracy. Then the equations for the constant-energy surfaces near this point have a more complicated form than we have assumed:

$$\epsilon = \epsilon_k + (\mathbf{p} - \mathbf{p}_k)^2 \varphi(\mathbf{n}),$$

where  $\varphi(\mathbf{n})$  is a function of the unit vector  $\mathbf{n} = (\mathbf{p} - \mathbf{p}_k)/|\mathbf{p} - \mathbf{p}_k|$ , appropriate to the symmetry at the point  $\mathbf{p} = \mathbf{p}_k$ . The conclusion about the nature of the singularity for  $\epsilon = \epsilon_k$  remains exactly the same.<sup>[50]</sup>

In the preceding section we considered the case of intersection of constant-energy surfaces. We note that for energies at which intersection occurs, the density of electron states has, of course, no singularities. In this case too those energies are singular or critical for which the topology of the constant-energy surfaces changes. For example, surfaces a and b in Fig. 7 are singular in this sense. It is easy to show that in these cases also  $\delta\nu(\epsilon)$  is  $\sim |\epsilon - \epsilon_k|^{1/2}$  and is different from zero only on one side of  $\epsilon_k$ .

The singular cases considered here (formation of new sheets at a point and breaking of a bridge at a point) exhaust all the types of singular points in  $\mathbf{p}$ -space.

But cases are possible where in certain approximations an extremum is reached not at isolated points but along a whole curve (belt of extrema). For example, in crystals of the wurtzite type the band of extrema is a circle with its center on the symmetry axis. A similar situation also occurs in other crystals (CdS, InSb etc).

Let us see what the density of electron states  $\nu(\epsilon)$  looks like for energies near the extremal values.

To be specific we consider crystals of the wurtzite type. According to <sup>[16]</sup>, the dispersion law for electrons with energies close to the extremal values has the form

$$\epsilon^\pm(\mathbf{p}) = Ap_1^2 + Bp_2^2 \pm ap_1. \quad (2.13)$$

Here  $p_1 = \sqrt{p_x^2 + p_y^2}$ , while the  $z$  axis coincides with



the crystal axis. The constant-energy surfaces corresponding to the first branch [the plus sign in (2.13)] are spheroids with their centers at the origin, while those corresponding to the second branch [the minus sign in (2.13)] are toruses with elliptical cross sections in planes passing through the symmetry axis (Fig. 11). Calculating the volume and differentiating with respect to the energy, we find the density of electron states:

for the first branch

$$v^+(\epsilon) \sim \begin{cases} \epsilon^{1/2}, & \epsilon > 0, \\ 0, & \epsilon < 0; \end{cases}$$

for the second branch

$$v^-(\epsilon) \sim \begin{cases} \frac{\pi\alpha}{BA^{3/2}}, & \epsilon > \epsilon_k = \frac{\alpha^2}{4A}, \\ 0, & \epsilon < \epsilon_k. \end{cases}$$

We note that the first branch starts at zero energy, and the second at  $\epsilon = \epsilon_k = \alpha^2/4A$ . Thus in this case at  $\epsilon = \epsilon_k$  the density of electron states has a finite jump. The size of the jump is determined by the parameter  $\alpha$ , which is related to the spin interaction of the electrons.

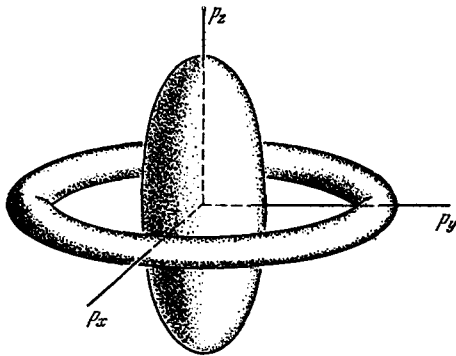


FIG. 11. Constant-energy surface for crystals with a belt of extrema, according to (2.13).

### 3. THERMODYNAMICS OF CONDUCTION ELECTRONS

Knowledge of the density of electron states enables us to construct a thermodynamics of the conduction electrons.

As we said earlier, the structure of the electron energy spectrum of a metal in the non-superconducting state is such that the charged elementary excitations, which we call conduction electrons, are a gas of quasi-particles subject to Fermi-Dirac statistics. This means that the equilibrium distribution function for the electrons  $n_F(\epsilon)$  is the Fermi function

$$n_F(\epsilon) = \frac{1}{e^{\epsilon - \zeta/T} + 1}, \tag{3.1}$$

where  $T$  is the temperature, measured in ergs, and  $\zeta$  is the chemical potential, defined by the normalization condition

$$N = \sum_s \int \frac{v_s(\epsilon) d\epsilon}{e^{\epsilon - \zeta/T} + 1}. \tag{3.2}$$

The integration can be taken over all energies, since  $v_s(\epsilon) \neq 0$  only within the  $s$ -th energy zone.

It is convenient to start developing the thermodynamics from the thermodynamic potential

$$\Omega = -T \sum_s \int v_s(\epsilon) \ln(e^{\epsilon - \zeta/T} + 1) d\epsilon, \tag{3.3}$$

or, after integration by parts,

$$\Omega = - \sum_s \int \frac{N_s(\epsilon) d\epsilon}{e^{\epsilon - \zeta/T} + 1}. \tag{3.4}$$

On the other hand, the total energy of the electron gas is

$$E = \sum_s \int \frac{\epsilon v_s(\epsilon) d\epsilon}{e^{\epsilon - \zeta/T} + 1}. \tag{3.5}$$

A comparison of formulas (3.4) and (3.5) shows that the relation  $PV = 2/3E$ , where  $P$  is the pressure (remember that  $\Omega = -PV$ ), holds only for free electrons, for which  $\nu(\epsilon) = dN/d\epsilon \sim \epsilon^{1/2}$  [cf. (2.7)].

Since  $\Omega = -PV$ , Eqs. (3.2) and (3.4) can be regarded as the parametric form of the equation of state of a gas of conduction electrons, where the parameter is the chemical potential  $\zeta$ . As we see from these formulas, the equation of state depends essentially on the density of states  $\nu(\epsilon)$ , i.e., on the dispersion law.

Now we shall consider the most important case of low temperatures, i.e., we shall assume that in all zones (for any  $s$ ) the electron gas is highly degenerate.

The degeneracy condition is formulated very simply in the case of the free electron gas ( $T \ll \epsilon_F$ ). In the case of conduction electrons, which have a complicated dispersion law, the condition for degeneracy means that

$$T \ll \min | \epsilon_F - \epsilon_k^{(s)} |, \tag{3.6}$$

where the  $\epsilon_k^{(s)}$  are singular (critical, extremal) values of the energy.

If condition (3.6) holds, in computing integrals which contain the Fermi function  $n_F(\epsilon)$  one can use the familiar expansion in powers of the temperature

$$\int \varphi(\epsilon) n_F(\epsilon) d\epsilon \cong \int_0^{\zeta} \varphi(\epsilon) d\epsilon + \frac{\pi^2}{6} T^2 \left( \frac{d\varphi}{d\epsilon} \right)_{\epsilon=\zeta} + \dots \tag{3.7}$$

From expressions (3.4), (3.7), and (2.6), we have

$$\Omega = \Omega_0 - \frac{\pi^2}{6} v(\zeta) T^2 + \dots, \quad v(\zeta) = \sum_s v_s(\zeta), \tag{3.8}$$

where the summation in the last expression is to be taken over overlapping, partially filled bands. The quantity  $\Omega_0$  is the value of the thermodynamic potential  $\Omega$  at  $T = 0$ :

$$\Omega_0 = - \sum_s \int_0^{\zeta} N_s(\epsilon) d\epsilon. \quad (3.8')$$

Treating the second term in (3.8) as a small correction to  $\Omega_0$  and expressing  $\zeta$  in terms of the electron density, using the zeroth approximation [i.e., stated simply, replacing the chemical potential  $\zeta$  by the limiting energy  $\epsilon_F$ , which is related to the electron density by formula (1.3)], we can write for the free energy  $F$

$$F = F_0 - \frac{\pi^2}{6} \nu(\epsilon_F) T^2 + \dots, \quad F_0 = N\epsilon_F - \sum_s \int_0^{\epsilon_F} N_s(\epsilon) d\epsilon. \quad (3.9)$$

We then find the entropy  $S_e$  and specific heat  $C_e$  of the conduction electron gas\*

$$S_e \simeq \frac{\pi^2}{6} \nu(\epsilon_F) T, \quad C_e \simeq \frac{\pi^2}{6} \nu(\epsilon_F) T. \quad (3.10)$$

Thus the electronic specific heat  $C_e$  at low temperatures [cf. condition (3.6)] depends linearly on temperature. This conclusion is independent of the dispersion law for the conduction electrons. Moreover, formula (3.10) remains valid even if we include the interaction between electrons in the spirit of the Landau theory of the Fermi liquid.<sup>[2]</sup>

From formulas (3.8), (3.9), and (3.10), it is easy to find approximate expressions for the energy  $E$  and the thermodynamic potential  $\Phi$  of the conduction electron gas:

$$E \simeq E_0 + \frac{\pi^2}{6} \nu(\epsilon_F) T^2, \quad E_0 = \int_0^{\epsilon_F} \epsilon \nu(\epsilon) d\epsilon, \quad (3.11)$$

$$\Phi \simeq \Phi_0 - \frac{\pi^2}{6} \nu(\epsilon_F) T^2, \quad \Phi_0 = N\epsilon_F. \quad (3.12)$$

The last expression enables us to determine the thermal expansion coefficient  $\alpha$ , equal to  $-(1/V)(\partial V/\partial T)_P$ :

$$\alpha \simeq \frac{\pi^2}{3} V^{-1} \frac{\partial}{\partial P} \nu(\epsilon_F) T. \quad (3.13)$$

We note that formula (3.13) is no less general than (3.10). In particular, formula (3.13) holds even when the electron interactions are included. In fact,  $\alpha \sim \partial^2 \Phi / \partial T \partial P = \partial^2 \Phi / \partial P \partial T = \partial S / \partial P$ , while the entropy of the electrons, being a quantity with a combinatorial significance, is determined by the systematics of the states, and these do not change when we go from the Fermi gas to the Fermi liquid.

For most metals the condition for degeneracy is satisfied at practically all temperatures. Thus the conduction electrons make an extremely small contribution to the thermodynamic quantities for the metal (specific heat, internal energy, etc). However, at low temperatures, when the internal energy of the vibrational degrees of freedom tends rapidly to zero ( $\sim T^4$ ),

\*For the temperature as defined here (in ergs) the specific heat is a dimensionless quantity.

the role of the conduction electrons grows rapidly in importance. At temperatures\*  $T \ll \theta \sqrt{\theta/\epsilon_F}$ , where  $\theta$  is the Debye temperature, the conduction electrons determine the thermodynamic properties of metals. In particular, this means that the specific heat of a metal and its thermal expansion coefficient depend linearly on temperature if the temperatures are sufficiently low. This is well known from both experimental and theoretical investigations.

The constant  $\gamma$  in the Grüneisen "law" (i.e., the temperature-independent ratio of the thermal expansion coefficient  $\alpha$  to the specific heat  $C$ ) for metals in this temperature range is determined by the dependence of the density of electron states on pressure †

$$\gamma \simeq 2 \frac{\partial}{\partial P} \ln \nu(\epsilon_F). \quad (3.14)$$

As we see from formula (3.10), the measurement of the specific heat of metals at low temperatures permits the determination of a very important characteristic of the electron energy spectrum, the density of electron states at the Fermi energy.

Now we study the temperature dependence of various thermodynamic characteristics of metals when the Fermi surface is close to singular points in  $p$ -space.

If the Fermi surface is close to the minimum (or maximum) point of one of the overlapping zones, this means that in this zone the number of occupied states—the number of electrons (or the number of free states—the number of holes) is small. Although the chemical potential  $\zeta$ , which is common to all the zones, depends very little on temperature, the number of electrons (or "holes") in the anomalously filled band considered here depends strongly on the temperature. In fact, from (3.2), noting that  $N$  is independent of temperature, we have

$$\zeta \simeq \epsilon_F - \frac{\pi^2}{6} \frac{\nu'(\epsilon_F)}{\nu(\epsilon_F)} T^2. \quad (3.15)$$

The number of electrons in the  $s$ -th band is

$$N_s(T) = \int \frac{\nu_s(\epsilon) d\epsilon}{e^{e^{-\zeta(T)/T} + 1}}. \quad (3.16)$$

We use the symbol  $\epsilon_{s0}$  for the minimum value of the energy in the  $s$ -th band if the band is almost empty, or for the maximum value if the band is almost full. The anomaly consists in having  $|\epsilon_F - \epsilon_{s0}| \ll \nu(\epsilon_F)/\nu'(\epsilon_F)$ . ‡

From (3.16), (3.15), and (3.7), we have

\*We assume for an estimate that  $\nu(\epsilon_F) \sim N/\epsilon_F$ , while  $N \sim \mathfrak{N}$ .

†At temperatures  $\theta \sqrt{\frac{\theta}{\epsilon_F}} \ll T \ll \theta$ , the Grüneisen constant, naturally, is determined by the pressure dependence of the Debye temperature.

‡The quantity  $\nu(\epsilon_F)/\nu'(\epsilon_F)$  characterizes the distance (in energy) between the Fermi surface and the singular constant-energy surfaces of the principal (non-anomalous) bands.

$$N_s(T) \simeq \begin{cases} N_s(0) + \frac{\pi^2}{6} \nu_s(\epsilon_F) T^2 \frac{d}{d\epsilon_F} \ln \left[ \frac{\nu_s(\epsilon_F)}{\nu(\epsilon_F)} \right] & (T \ll |\epsilon_F - \epsilon_{s0}|), \\ N_s(0) \frac{3(\sqrt{2}-1)}{4\sqrt{2}} \sqrt{\pi} \zeta\left(\frac{3}{2}\right) \left( \frac{T}{|\epsilon_F - \epsilon_{s0}|} \right)^{3/2} \left( \frac{\nu(\epsilon_F)}{\nu'(\epsilon_F)} \gg T \gg |\epsilon_F - \epsilon_{s0}| \right). \end{cases} \quad (3.17)$$

In obtaining the last formula we have used the fact that, according to (2.8) and (2.8'),  $\nu_s(\epsilon) \sim |\epsilon - \epsilon_{s0}|^{1/2}$ .

Knowledge of the temperature dependence of the number of electrons in the anomalous band is important in those cases where the properties of the metal are determined by the electrons in the anomalous bands (for example, the diamagnetism of various metals<sup>[17]</sup>).

In the first section we spoke of hypothetical solids in which the Fermi surface was a point (in such bodies there is no energy gap between the filled and empty bands). The thermodynamic properties of the electrons in such bodies are determined by the dispersion law near the point of contact of the bands. For example, if the dependence of the energy on quasimomentum near the boundary of the zones is quasilinear ( $\epsilon \sim p$ ), the contribution of the electrons to the specific heat of the metal is proportional to  $T^3$ , but if the dependence is quadratic ( $\epsilon \sim p^2$ ),  $C_e \sim T^{3/2}$ . However, one should remember that interaction of the electrons, as a rule, removes such a degeneracy, so that an energy gap appears between the bands, which makes such bodies ordinary semiconductors.

#### 4. ANOMALIES OF ELECTRONIC PROPERTIES OF A METAL AT HIGH PRESSURES<sup>[18]</sup>

As we have already said (Sec. 2) a change in the topology of the constant-energy surfaces results in a singularity of the density of states  $\nu(\epsilon)$ . Generally speaking the values  $\epsilon_k$  are located quite far from the limiting Fermi energy  $\epsilon_F$ , and the presence of the singular points  $\epsilon_k$  can be discovered only from x-ray spectra. But if there is some continuously varying parameter, in the course of whose variation  $\epsilon_F - \epsilon_k$  passes through zero, i.e., if one can change the topology of the Fermi surface, the singularities of the spectral density  $\nu(\epsilon)$  and the dynamics of the electrons near the "critical" surface lead to peculiar anomalies in the thermodynamic and kinetic characteristics of the electron gas in a metal.

Such a continuous parameter may be deformation of the lattice, in particular, uniform compression at high pressures. It is known that at high pressures the anisotropy of most properties decreases, so one may anticipate for example that a Fermi surface of the "crimped cylinder" type, which is characteristic of layered structures, should, as it deforms, gradually go over into a closed surface, even when the total number of electrons in the conduction band is constant (Fig. 12). Naturally, other changes in the topology of the Fermi surface are also possible. It should be emphasized

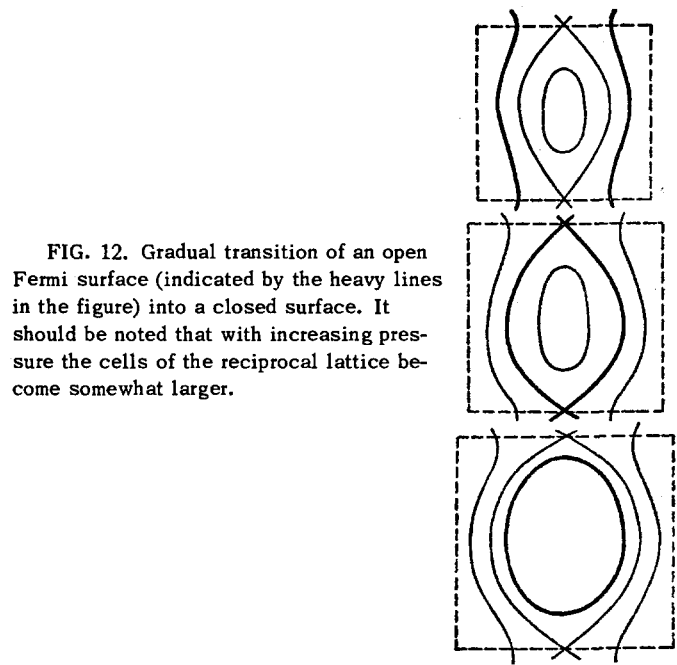


FIG. 12. Gradual transition of an open Fermi surface (indicated by the heavy lines in the figure) into a closed surface. It should be noted that with increasing pressure the cells of the reciprocal lattice become somewhat larger.

that a change in the topology of the Fermi surface is not accompanied by a change in the symmetry of the lattice and so does not give rise to a second-order phase transition.

On the other hand, the initial lattice may cease to be thermodynamically stable even before arriving at the "critical" Fermi surface, so that a first-order phase transition occurs before the appearance of the anomalies associated with a change of the topology.\* But because the time for "readjustment" of the electrons during deformation of a metal is short compared to the time for rearrangement of the lattice during a phase transition, such anomalies can also be observed in the short-lived metastable state; for this reason we need not be concerned with the question whether the state is stable or metastable near the point where the topology of the Fermi surface changes.

Another parameter, the concentration of impurities or of the components of an alloy, might seem to have a stronger effect on the chemical potential  $\zeta$  and the Fermi surface; for a disordered lattice the very concept of the Fermi surface ceases to have any precise meaning, so the singularities of  $\nu(\epsilon)$  are smeared out and actually do not exist.

\*In particular this case occurs in so-called isomorphic transitions, in which the lattice parameters change abruptly while the type of structure remains unchanged.

In the following we shall investigate the properties of a metal in the vicinity of an "electronic transition" caused by a change in the topology of the Fermi surface.

If the chemical potential  $\zeta$  is close to  $\epsilon_k$ , then in accordance with formulas (3.4) and (2.9) the thermodynamic potential  $\Omega$  will have the following form:

$$\Omega(\zeta, T) = \Omega_0(\zeta, T) + \delta\Omega, \quad (4.1)$$

where

$$\delta\Omega = - \int_0^\infty \frac{\delta N(\epsilon) d\epsilon}{e^{\epsilon - \zeta/T} + 1}, \quad (4.2)$$

and

$$\delta N = \begin{cases} 0 & (\epsilon < \epsilon_k), \\ \frac{2}{3} \alpha (\epsilon - \epsilon_k)^{3/2} & (\epsilon > \epsilon_k). \end{cases} \quad (4.3)$$

The significance of the parameter  $\alpha$  is clear from formulas (2.10) and (2.6). To be specific we assume that the new sheet appears for  $\epsilon > \epsilon_k$ . Setting  $\epsilon - \epsilon_k = x$  and  $\zeta - \epsilon_k = z$ , we find that at low temperatures ( $T \ll z$ ) near the point  $z = 0$  the variation in the thermodynamic potential can be represented as follows:

$$\delta\Omega = \begin{cases} -\frac{\pi}{2} \alpha T^{3/2} e^{-|z|/T}, & \text{(I)} \\ -\frac{4}{15} \alpha |z|^{5/2} - \frac{\pi^2}{6} \alpha T^2 |z|^{1/2}. & \text{(II)} \end{cases} \quad (4.4)$$

The transition from region (I) to region (II) corresponds to the appearance of a new sheet on the surface  $\epsilon(\mathbf{p}) = \zeta$  (or a reduction of its connectivity).

The formulas (4.4) are valid for  $T \ll |z|$ . At absolute zero

$$\delta\Omega = \begin{cases} 0, & \text{(I)} \\ -\frac{4}{15} \alpha |z|^{5/2}. & \text{(II)} \end{cases} \quad (4.5)$$

This means that the second derivatives of  $\Omega$  at the point  $z = 0$ , which is the point at which the "electronic transition" occurs, have a vertical kink, while the third derivatives go to infinity like  $z^{-1/2}$ .

Since the number of electrons in the conduction band is constant, to determine the anomalies in thermodynamic quantities it is convenient to use instead of the potential  $\Omega$  the free energy  $F = F(T, V, N)$ . The volume  $V$  is then the parameter associated with the applied pressure; the critical energy  $\epsilon_k$  is a function of the volume  $\epsilon_k = \epsilon_k(V)$ , while the chemical potential  $\zeta$  is also a function of  $V$  because of the constancy of the number of particles\*:

$$N(\zeta, V) = N. \quad (4.6)$$

We shall use  $V_k$  to denote the volume at which the change in the topology of the Fermi surface occurs, i.e.,

\*In the case where there are several overlapping bands,  $N(\zeta, V)$  is the total number of particles in all the bands.

$$\zeta(V_k) = \epsilon_k(V_k). \quad (4.7)$$

According to (4.6) and (4.7), the modulus of  $z$ , which appears in formulas (4.4) and (4.5), can be expressed in terms of  $|V - V_k|$ :

$$z = \gamma |V - V_k|, \quad \gamma = \left| v^{-1}(\epsilon_k) \left\{ \frac{\partial N}{\partial V} + v(\epsilon_k) \frac{d\epsilon_k}{dV} \right\} \right|, \quad (4.8)$$

where we have used the fact that  $\partial N / \partial \zeta = \nu(\zeta)$ .

Writing the free energy  $F$  in the form

$$F = F_0 + \delta F,$$

where  $F_0$  is the smoothly varying part of the free energy, constructed using the density  $\nu_0(\epsilon)$ , it is easy to show that  $\delta F$  is equal to the irregular correction  $\delta\Omega$ , expressed in terms of the variables  $V$  and  $T$ , i.e.,  $\delta F$  is given by formulas (4.4) and (4.5), with  $|z|$  replaced by its value from (4.8):

$$\delta F = \begin{cases} -\frac{\sqrt{\pi}}{2} \alpha T^{3/2} e^{-z/T}, & \text{(I)} \\ -\frac{4}{15} \alpha |z|^{5/2} - \frac{\pi^2}{6} \alpha T^2 |z|^{1/2} & \text{(II)} \end{cases} \quad (T \ll |z|, |z| = \gamma |V - V_k|).$$

When the temperature tends to absolute zero, we get

$$\delta \frac{C_e}{T} = -\delta \frac{\partial^2 F}{\partial T^2} = \begin{cases} 0, & \text{(I)} \\ \frac{\pi^2}{3} \alpha |z|^{1/2}, & \text{(II)} \end{cases} \quad (4.9)$$

$$\delta \frac{\partial P}{\partial V} = -\delta \frac{\partial^2 F}{\partial V^2} = \begin{cases} 0, & \text{(I)} \\ \alpha \gamma^2 |z|^{1/2}, & \text{(II)} \end{cases} \quad (4.10)$$

$$\delta \left( \frac{\partial P}{\partial T} / T \right) = -\frac{1}{T} \delta \frac{\partial^2 F}{\partial T \partial V} = \begin{cases} 0, & \text{(I)} \\ \frac{\pi^2}{3} \alpha \gamma |z|^{-1/2}. & \text{(II)} \end{cases} \quad (4.11)$$

Expression (4.9) describes the anomaly in the electronic specific heat; (4.10) gives the anomaly in the electronic compressibility.

The total pressure in a metal is made up of the electron pressure and the partially compensating pressure of the lattice "skeleton" of the metal. Since, however, the lattice part of the compressibility  $\partial P_l / \partial V$  is generally continuous at the point  $z = 0$ \*, the singularity in the total compressibility is given by the same equation.

Finally, as one sees from (4.11), the sharpest singularity occurs for the temperature coefficient of the pressure,  $\partial P / \partial T$ . Since at low temperatures the electronic part of this coefficient is the most important, we have for the smoothly varying part

$$\left( \frac{\partial P}{\partial T} \right)_V = AT, \quad A = \frac{\pi^2}{3} \frac{\partial \nu}{\partial V}.$$

Thus in the region of the anomaly

\*It may happen that the part of the "lattice" binding energy which is due to the conduction electrons has a singularity at the point  $z = 0$  of the same character as  $\Omega_e$ ; this would give a negligible correction to  $\partial P / \partial V$ , and would not change our results qualitatively.

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\pi^2}{3} T \left\{ \frac{\partial v}{\partial V} \pm \frac{1}{2} \alpha \gamma z^{-1/2} \right\}, \quad (\text{II}) \quad (4.12)$$

where the plus sign holds when  $V - V_k > 0$  in region (II), and the minus sign when  $V_k - V > 0$  in (II). The thermal expansion coefficient  $(\partial V/\partial T)_P = -(\partial P/\partial T)_V / (\partial P/\partial V)_T$  has the same singularity:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\pi^2 T}{3\kappa_0} \left\{ \frac{\partial v}{\partial V} \pm \frac{1}{2} \alpha \gamma |z|^{-1/2} \right\}, \quad (\text{II})$$

$$\kappa_0 = -\left(\frac{\partial P}{\partial V}\right)_{T=0}. \quad (4.13)$$

We note in particular that if a new sheet appears for  $P = P_k$ , as the pressure is increased, the thermal expansion coefficient in the neighborhood of  $P = P_k$  ( $V = V_k$ ) is negative on the high pressure side and increases to infinity in absolute value for  $P \rightarrow P_k$  (Fig. 13).

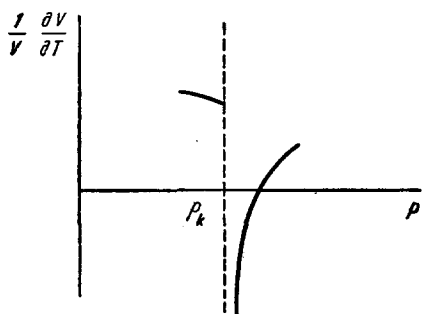


FIG. 13. Behavior of the thermal expansion coefficient (for  $T = 0$ ) in the neighborhood of the critical pressure  $P_k$ , if the number of sheets of the Fermi surface increases at  $P = P_k$ .

In order to treat all the formulas (4.9)–(4.11) as anomalies in the pressure scale, we simply use the fact that  $P - P_k = -\kappa_0(V - V_k)$ , and consequently

$$|z| = |\gamma| |V - V_k| = \frac{|\gamma|}{\kappa_0} |P - P_k|. \quad (4.14)$$

It is convenient to estimate the coefficients  $\gamma$ ,  $\gamma/\kappa_0$  and the critical pressure  $P_k$  by expressing them in terms of the initial energy difference  $z_0 = (\xi - \epsilon_k)_{P=0}$  (at zero pressure) and the critical deformation  $(V - V_k)/V_0$ , at which the transition occurs,

$$|z| = \frac{|z_0| |P - P_k|}{P_k}, \quad P_k = \kappa_0 |V - V_k|, \quad \gamma = \frac{z_0}{|V_0 - V_k|}. \quad (4.15)$$

It is understood that (4.15) is only an estimate, since over a large range of deformations the linear relation between  $P$  and  $V - V_0$  breaks down. If we assume for the critical deformation  $(V_0 - V_k)/V_0 \sim 0.05-0.1$ ,  $P_k \sim 5 \times 10^4 - 10^5 \text{ kg/cm}^2$ .\*

Strictly speaking, formulas (4.9)–(4.11) are valid

\*It might seem that less symmetric deformations (such as uniaxial compression or tension) change the geometry of the Fermi surface more strongly and require lower stresses. In particular, violation of the initial symmetry of the crystal at arbitrarily small deformations may lead to the splitting off of the surface at points where it must intersect itself.

at absolute zero. At finite temperatures the singularities of all thermodynamic quantities are smeared out. The width of the temperature smearing of the anomaly is  $\Delta z \sim T$ ; on the pressure scale this gives

$$\frac{\Delta P}{P_k} \sim \frac{T}{|z_0|} = \frac{T}{|\xi - \epsilon_k|_{P=0}}. \quad (4.16)$$

From formula (4.10) it follows that in the region of the anomaly a positive correction  $\sim z^{1/2}$  is added to the negative quantity  $(\partial P/\partial V)_0 = -\kappa_0$ . If as a result  $P(V)$  ceases to be a monotonic function and  $\partial P/\partial V$  becomes positive over some region, an isomorphic phase transition of the first kind takes place with a jump in the volume. Writing the expansion of  $\partial P/\partial V$  for small positive  $z$  and temperature approaching absolute zero:

$$\frac{\partial P}{\partial V} = -\kappa_0 + \alpha \gamma^2 z^{1/2} - \kappa_1 z,$$

we see that a region of instability ( $\partial P/\partial V > 0$ ) can occur if  $\alpha \gamma^2 > 2\sqrt{\kappa_0 \kappa_1}$ ; it lies to the right of the point  $z = 0$  in the interval

$$\alpha \gamma^2 - \sqrt{(\alpha \gamma^2)^2 - 4\kappa_0 \kappa_1} < 2\kappa_0 z < \alpha \gamma^2 + \sqrt{(\alpha \gamma^2)^2 - 4\kappa_0 \kappa_1}.$$

The point  $z = 0$  where the electronic transition occurs lies in the region of metastability or stability.

Since at finite temperatures the singularity at  $z = 0$  is smeared out, the electronic transition at  $z = 0$  should not be called a phase transition; we shall therefore always speak of “anomalies” at the point  $z = 0$ , although according to Ehrenfest’s terminology one could provisionally call such anomalies at  $T = 0$  “ $2^{1/2}$ -order transitions,” since the second derivatives of the thermodynamic potentials have a singularity  $\sim z^{1/2}$ , and the third derivatives a singularity  $\sim z^{-1/2}$ .

In the second section we stated that cases are possible where the density of electron states jumps abruptly at some energy  $\epsilon = \epsilon_k$ . If, because of compression (or some other deformation of the lattice) the limiting Fermi energy coincides with  $\epsilon_k$ , this should manifest itself in a jump in the electronic specific heat and the other second derivatives of the thermodynamic potential. In this admittedly very special case, the electronic anomaly would look very much like a second-order phase transition.

Electronic anomalies due to a change in the topology of the Fermi surface should affect the magnetic properties of a metal and should appear particularly clearly in the behavior of the galvanomagnetic characteristics.<sup>[18]</sup>

## 5. PARA- AND DIAMAGNETISM (WEAK MAGNETIC FIELDS)

If a metal is placed in a magnetic field, many of its properties are drastically changed. For example, the resistance of pure metals increases by a factor of ten and sometimes even by a factor of 100 or 1000 at low temperatures in a magnetic field of a few kOe. As a rule the kinetic coefficients (resistivity, thermal conductivity etc) of metals suffer large changes. But the

thermodynamic equilibrium values of metal characteristics also change under the action of a magnetic field. In particular, all metals in a magnetic field have a magnetic moment, which at low temperatures in large fields depends in a complicated way on the magnitude and direction of the magnetic field.

The dependence of thermodynamic quantities on magnetic field is due<sup>[19]</sup> to the quantization of the energies of electrons and nuclei. With respect to electrons, this remark applies both to conduction electrons and to electrons with a complex dispersion law. In fact in a classical treatment the inclusion of the magnetic field corresponds to changing to the kinetic momentum  $\mathbf{p} = \mathbf{P} - e/c\mathbf{A}$  (the notation is the same as in <sup>[1]</sup>). In computing the thermodynamic potentials, the integration is extended over all of  $\mathbf{P}$ -space. Changing the variables (from  $\mathbf{P}$  to  $\mathbf{p}$ ), we see that the thermodynamic potentials are independent of the magnetic field.

In the quantum treatment, a dependence on magnetic field appears for two reasons. First, the electrons and nuclei have intrinsic (spin) magnetic moments\* and, second, the orbital (spatial) motion of the charged particles in the magnetic field is quantized. The presence of intrinsic magnetic moments is the origin of paramagnetism and related phenomena, while the quantization of the orbital motion gives rise to diamagnetism.

The main quantity which is to be examined in this section is the magnetic moment of the metal. The magnetic moment of the metal does not arise simply from the contribution of the conduction electrons (i.e., the electrons in partially filled bands). Even if we disregard the nuclei, whose contribution is very small because the nuclear magnetic moments are small, there are still the filled bands which participate in the formation of the diamagnetic moment.† The diamagnetic susceptibility of the electrons in a metal can be expressed in terms of the dispersion law,<sup>[20]</sup> but the resulting expression is complicated and hard to visualize. Besides, as we said in the Introduction, the very concept of a dispersion law is applicable only near the Fermi surface. So it is obvious that there is no justification for attributing great significance to expressions which depend on the properties of electrons whose energies are much less than the Fermi energy.

Electrons in filled shells have compensated spins.‡

\*We remind the reader that the presence of an intrinsic magnetic moment is a quantum effect. Its magnitude contains the Planck constant:  $\mu_0 = e\hbar/2m_0c$  (where  $\mu_0$  is the Bohr magneton and  $m_0$  is the free electron mass).

†The separation of the moment into paramagnetic and diamagnetic parts is possible only in weak fields, when the moment depends linearly on the magnetic field.

‡Such a band structure is typical for diamagnetic materials. In paramagnetic materials there are electrons with uncompensated spins in the filled bands (just as there are inner electrons with uncompensated spins in paramagnetic atoms). The exchange

The absence of empty states near the occupied ones results in an exponential dependence on temperature for the magnetic moment due to the electrons in the filled shells. Thus the main contribution to the paramagnetism of a metal comes from the conduction electrons (Pauli paramagnetism).

It is known<sup>[21]</sup> that the magnetic susceptibility ( $\kappa_p$ ) depends weakly on temperature, and at low temperatures ( $T \ll \epsilon_F$ ) is determined by the density of electrons per unit energy range at the Fermi energy:

$$\kappa_p = \mu^2 \nu(\epsilon_F). \quad (5.1)$$

This formula is derived on the "gas model" for the metal, i.e., omitting interaction of the electrons. Including the electronic interaction changes the formula (5.1) in the sense that the coefficient of  $\nu(\epsilon_F)$  cannot be taken to be  $\mu_0^2$ . It therefore seems natural not to attribute any significance to the comparison of (5.1) with experimental data on the paramagnetic susceptibility of metals.\*

The problem of comparing the theoretical results with experimental data is complicated still further by the fact that the diamagnetic and paramagnetic susceptibilities of metals are of the same order. For example, for a gas of free electrons the diamagnetic susceptibility is one third the paramagnetic. The fact that the two susceptibilities have the same order of magnitude is a direct consequence of the degeneracy of the electron gas ( $T \ll \epsilon_F$ ).

As we see from (5.1), the paramagnetic susceptibility of a metal is proportional to the density of electron states per unit energy interval (at the energy  $\epsilon = \epsilon_F$ ). This means that the spin paramagnetism suffers an anomaly when the topology of the Fermi surface changes under the influence of the pressure (cf. Sec. 4 and also <sup>[18]</sup>). Let us examine the nature of this anomaly.

In an external magnetic field, the spin magnetic moment is

$$M_\sigma = \frac{1}{2} \mu_{ef} \{N(\zeta + \mu H) - N(\zeta - \mu H)\},$$

where  $N(\epsilon)$  is the number of electrons with energies less than  $\epsilon$  (cf. Sec. 2). Then the paramagnetic susceptibility  $\kappa_p$  in the vicinity of the anomaly has the form

$$\kappa_p = \kappa_p^{(0)} + \frac{1}{2} \mu_{ef}^2 \{\delta \nu(\zeta + \mu H) + \delta \nu(\zeta - \mu H)\},$$

where

---

interaction between the spins, as a rule, leads to their ordering, i.e., to the appearance at sufficiently low temperatures of either ferromagnetism or antiferromagnetism.

\*Furthermore, one should remember that for crystals with strong spin-orbit coupling, the structure of the paramagnetic levels may be significantly different from the structure of the levels of the free electron.<sup>[22]</sup> In particular, in this case the state of the electron in the magnetic field is not characterized by a definite projection of the spin along the magnetic field.

$$\delta v(z) = \begin{cases} 0 & (z < 0), \\ \alpha z^{1/2} & (z > 0). \end{cases}$$

The significance of the parameter  $\alpha$  is clear from formula (2.8). Thus the irregular part of the paramagnetic susceptibility  $\delta\kappa_p$  is:

$$\delta\kappa_p = \begin{cases} 0, & z + \mu H < 0, \quad z - \mu H < 0; \\ \frac{1}{2} \alpha \mu_{\text{ef}}^2 (z + \mu H)^{1/2}, & z + \mu H > 0, \quad z - \mu H < 0; \\ \frac{1}{2} \alpha \mu_{\text{ef}}^2 (z - \mu H)^{1/2}, & z + \mu H < 0, \quad z - \mu H > 0; \\ \frac{1}{2} \alpha \mu_{\text{ef}}^2 \{ (z + \mu H)^{1/2} + (z - \mu H)^{1/2} \}, & z + \mu H > 0, \quad z - \mu H > 0. \end{cases}$$

Although the actual picture of the anomaly in the magnetic susceptibility of the metal is somewhat complicated by the presence of the diamagnetism, the qualitative picture is naturally the same. In particular one should note the sharp irregular dependence of the magnetic susceptibility on magnetic field in the vicinity of the critical pressure. True, this irregularity must be observed in an extremely narrow pressure interval  $\Delta p \sim (\mu H / \epsilon_F) p_k$ .

The dependence of  $\delta\kappa_p$  on  $z$  and magnetic field is shown in Fig. 14.

The presence of singularities of the magnetic susceptibility at high pressures is not the only manifestation of the peculiar features of the electron energy spectrum in the behavior of metals in weak fields.

The temperature dependence of the magnetic susceptibility of various metals (Bi, Sb, etc) can be treated only on the assumption that there are bands in the metal with anomalously small numbers of conduction electrons<sup>[17]</sup> (cf. also the end of Sec. 3).

## 6. THE DE HAAS-VAN ALPHEN EFFECT (STRONG MAGNETIC FIELDS)

In the preceding section it was shown that one cannot describe the magnetic properties of metals using only noninteracting conduction electrons. However, as we have already said, most metals have specific oscillational properties in high fields ( $\mu H \gtrsim T$ ). As we shall see, the electrons with energies of the order of the Fermi energy ( $\epsilon \sim \epsilon_F$ ) are responsible for these oscillational properties.

The best-investigated of the oscillational effects is the de Haas-van Alphen effect, i.e., the complicated dependence of magnetic moment on magnetic field which is observed at low temperatures in strong fields ( $\mu H \gtrsim T$ ).

This effect has been seen in a large number of metals and apparently is a specific metallic property, i.e., a property belonging to all metals.

Most of the oscillational properties (the Shubnikov-de Haas effect, et al) have the same nature as the de Haas-van Alphen effect (cf. Sec. 5 in [1]).

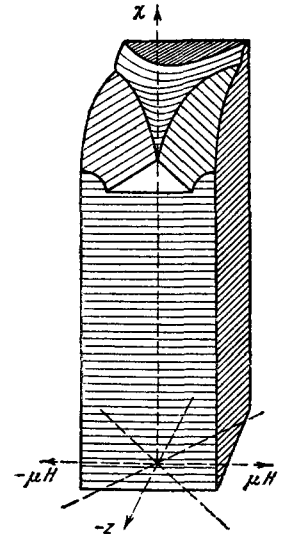


FIG. 14. Anomaly in the paramagnetic susceptibility near the point  $p = p_k$ .

All the characteristics of a body in equilibrium can be computed if we know its thermodynamic potential. Thus the main problem of this section will be the calculation of the oscillational part of the thermodynamic potential  $\Omega$  of the conduction electrons. The computation will be done in the "gas" approximation.<sup>[23]</sup> Later (in Sec. 7) we shall show that including interactions does not change the picture of the effect.

According to the general formulas of statistical thermodynamics

$$\Omega = -T \sum_{(S)} \ln \left\{ 1 + \exp \left\{ \frac{\xi - \epsilon_S}{T} \right\} \right\}. \quad (6.1)$$

The summation extends over all states of the electron,\* over the quantum number  $n$  [cf. Eq. (5.6) of [1]], over the two spin projections  $\sigma$  ( $\sigma = \pm 1$ ), over all values of the  $z$  component of the quasimomentum  $p_z$  and over the indices of the partially filled bands. Since  $p_z$  varies continuously, the summation over  $p_z$  can be replaced by an integration.

The number of states  $dn_{p_z}$  in the interval  $(p_z, p_z + dp_z)$  for fixed values of the other parameters  $(s, n, \sigma)$  is easily computed if we note that

$$dn_{p_z} = \frac{V}{(2\pi\hbar)^3} \left\{ \iint dp_x dp_y \right\} dp_z, \quad (6.2)$$

where the integration is to be taken over all values of  $p_x$  and  $p_y$  lying between neighboring classical trajectories of the electron in momentum space, i.e., between trajectories for which the values of  $n$  differ by unity. According to formula (5.6) of [1], this area is equal to  $-eH\hbar/c$ .

Thus

$$dn_{p_z} = - \frac{eHV}{(2\pi\hbar)^2 c} dp_z. \quad (6.3)$$

\*We are not considering the integration over coordinates, which reduces to multiplying by the volume  $V$  of the metal.

The use of the formula for quasiclassical quantization does not mean that (6.3) is valid only in the quasiclassical approximation. According to (6.2), the density of states  $dn_{p_z}/dp_z$  is determined by the "cell area" in  $p_x, p_y$ -space ( $\iint dp_x dp_y = \Delta p_x \Delta p_y$ ), which depends only on the commutation relations for the operators  $\hat{p}_x$  and  $\hat{p}_y$ . Using formula (6.19) of [1], we again arrive at formula (6.3).

Using the value of the density  $dn_{p_z}/dp_z$ , we can rewrite (6.1) in the following form:

$$\Omega = \sum_{n=0}^{\infty} \varphi(n), \quad (6.4)$$

where

$$\varphi(n) = \frac{VeHT}{(2\pi\hbar)^2 c} \sum_{\sigma, s} \int_{-\infty}^{\infty} \ln \left\{ 1 + \exp \frac{\zeta - \varepsilon_{s\sigma}(p_z, n)}{T} \right\} dp_z. \quad (6.5)$$

It will be convenient to use the Poisson formula [24]\*

$$\sum_{n_0}^{\infty} \chi(n) = \int_a^{\infty} \chi(n) dn + 2 \operatorname{Re} \sum_{k=1}^{\infty} \int_a^{\infty} \chi(n) e^{2\pi i k n} dn. \quad (6.5a)$$

In this formula,  $\chi(n)$  is an arbitrary function,  $a$  is a number between  $n_0 - 1$  and  $n_0$ . For our conditions,  $n_0 = 0$ , and it is convenient to set  $a = -1/2$ .

We then have from (6.4) and (6.5)

$$\Omega = \int_{-1/2}^{\infty} \varphi(n) dn + 2 \operatorname{Re} \sum_{k=1}^{\infty} \int_{-1/2}^{\infty} \varphi(n) e^{2\pi i k n}. \quad (6.6)$$

Further computations can be done only if one knows the dependence of the electron energy on the quantum numbers. We shall assume that†

$$\varepsilon_{\sigma}(p_z, n) = \varepsilon_n(p_z) + \sigma \mu_0 H \quad (\sigma = \pm 1), \quad (6.7)$$

where  $\varepsilon_n(p_z)$  is defined by the quasiclassical quantization conditions‡ (cf. (5.6) in [1])

$$S(\varepsilon, p_z) = \frac{e\hbar H}{c} \left( n + \frac{1}{2} \right). \quad (6.8)$$

For simplicity, we have dropped the subscript  $s$ .

The use of the quasiclassical energy levels (6.7) is justified by the fact that the main contribution to the oscillating part of the thermodynamic potential comes from electrons with large quantum numbers  $n$ , if the magnetic field is not too large:

\*The Poisson formula is easily obtained if we use the relation

$$\sum_{n=-\infty}^{\infty} \delta(x-n) = \sum_{k=-\infty}^{\infty} e^{2\pi i k x}.$$

This is simply the expansion of the periodic function  $\sum_{n=-\infty}^{\infty} \delta(x-n)$  in Fourier series.

†In the case of strong spin-orbit coupling,  $\mu_0$  may not be equal to the Bohr magneton. In this case the spin projection along the magnetic field is not a good quantum number.

‡As we shall see later, the main oscillational terms can be computed even neglecting the  $1/2$  in formula (6.8). However, we note that condition (6.8), including the  $1/2$ , remains valid for the case of an arbitrary dispersion law, and breaks down only near trajectories with self-intersections (cf. the footnote on p. 844 of [1], and also Sec. 3 of the Appendix).

$$\frac{cS}{e\hbar H} \gg 1. \quad (6.9)$$

We shall assume that this condition is always satisfied.

The first term in (6.6) describes the monotonic dependence of the thermodynamic potential on the magnetic field. The oscillatory dependence is contained in the other terms, which we shall study. In doing this we shall drop all the monotonic terms. We use the notation  $\tilde{\Omega}$  for the oscillatory part of  $\Omega$ .

According to (6.5) and (6.6)

$$\begin{aligned} \tilde{\Omega} &= \sum_{\sigma} \tilde{\Omega}_{\sigma}, \\ \tilde{\Omega}_{\sigma} &= 2 \operatorname{Re} \sum_{k=1}^{\infty} I_k, \end{aligned} \quad (6.10)$$

where

$$I_k = \frac{VeHT}{(2\pi\hbar)^2 c} \int_{-1/2}^{\infty} dn \int_{-\infty}^{\infty} dp_z \ln \left\{ 1 + \exp \frac{\zeta_{\sigma} - \varepsilon_n(p_z)}{T} \right\} e^{2\pi i k n}, \quad (6.11)$$

and

$$\zeta_{\sigma} = \zeta - \sigma \mu_0 H. \quad (6.12)$$

Expression (6.11) can be transformed if, using (6.8), we first change to an integration over the energy (in place of the integration over  $n$ ), and then replace the integration over  $p_z$  by an integration over  $n$ , again using (6.8). The result is

$$I_k = \frac{2\pi V}{(2\pi\hbar)^3} \int_0^{\infty} \frac{d\varepsilon}{e^{\varepsilon - \zeta_{\sigma}/T} + 1} \int_0^{\varepsilon} d\varepsilon' \sum_{n_{\min}}^{n_{\max}} \int \frac{n^* (\varepsilon', n)}{\left| \frac{\partial n}{\partial p_z} \right|} e^{2\pi i k n} dn. \quad (6.12')$$

The summation sign here denotes a summation over the intervals of monotonic variation of the function  $n(\varepsilon, p_z)$  for fixed  $\varepsilon$ .

The idea in the calculation to separate out the oscillatory dependence is to make use of the fact that all the quantities in the integral (6.12'), except for  $(e^{\varepsilon - \zeta_{\sigma}/T} + 1)^{-1}$  and  $e^{2\pi i k n}$ , vary slowly with  $\varepsilon$  and  $n$ . For  $\varepsilon \sim \zeta_{\sigma}$ , the quantities  $n_{\min}$  and  $n_{\max}$  as a rule are considerably larger than unity,\* i.e.,  $S_{\text{extr}} \cdot c/e\hbar H \gg 1$ . As shown in [1], this corresponds to the fact that an electron with energy close to the Fermi energy describes an area which is much greater than the square of the interatomic distance. This last condition corresponds to the condition for applicability of the quasiclassical approximation.

Since  $n \gg 1$ , one can use the saddle point method and show that the main contribution to the first integral comes from the vicinity of the extremal points  $n_m(\varepsilon')$ . After performing these computations, we get

$$I_k \approx \frac{VeHe^{-i\pi/2}}{2\pi c (2\pi\hbar)^2 k^{3/2}} \sum_m e^{\pm i\pi/4} \int_0^{\infty} \frac{e^{2\pi i k n_m(\varepsilon)}}{e^{\varepsilon - \zeta_{\sigma}/T} + 1} \frac{d\varepsilon}{\sqrt{\left| \frac{\partial^2 n}{\partial p_z^2} \right|_{p_{z,m}}} }. \quad (6.13)$$

\*At each energy value one has  $n_{\min} = 0$  (for that value of  $p_z$  at which the plane  $p_z = \text{const}$  is tangent to the constant-energy surface. These points are of no interest, since the integration in their vicinity gives no contribution to the oscillating part of the potential. [22])



The summation is over all the extremal points of the function  $n(\epsilon, p_z) = \frac{cS(\epsilon, p_z)}{ehH}$  for fixed  $\epsilon$ . The points at which  $n_m = 0$  are omitted. The plus sign in the expression  $e^{\pm i\pi/4}$  occurs when the extremal point is a minimum, and the minus sign when the extremal point is a maximum.

Now we make use of the fact that the main contribution to the oscillating part  $I_k$  comes from integration near the point of most rapid variation of the Fermi function, the point  $\epsilon = \zeta_\sigma$ . This enables us to write the last expression in the form:

$$I_k \approx \frac{VeH e^{-i\pi/2}}{2\pi c (2\pi\hbar)^2 k^{3/2}} \sum_m e^{-2\pi i k n_m(\zeta_\sigma) \pm i\pi/4} \times \frac{1}{\sqrt{\left| \frac{\partial^2 n}{\partial p_z^2} \right|_{\substack{\epsilon=\zeta_\sigma \\ p_z=p_z^m}}} \int_0^\infty \frac{e^{2\pi i k (dn_m/d\epsilon)_{\epsilon=\zeta_\sigma} (e-\zeta_\sigma)} e^{-\zeta_\sigma/T} + 1} d\epsilon.$$

Introducing the new integration variable  $x = \epsilon - \zeta_\sigma/T$  and using the fact that  $T \ll \zeta_\sigma$ , we extend the integration from  $-\infty$  to  $+\infty$ . After integrating and substituting the resulting expression into (6.10), we get

$$\tilde{\Omega} \approx \frac{V}{2\pi^3 \sqrt{2\pi\hbar^3}} \left( \frac{e\hbar H}{c} \right)^{3/2} \sum_m \left| \frac{\partial^2 S(\epsilon, p_z)}{\partial p_z^2} \right|_{\substack{\epsilon=\zeta \\ p_z=p_z^m}}^{-1/2} (m^*(\zeta, p_z^m))^{-1} \times \sum_{k=1}^\infty \frac{\Psi(k\lambda)}{k^{5/2}} \cos \left\{ k \left( \frac{cS_m}{e\hbar H} - \pi \pm \frac{\pi}{4} \right) \right\} \cos \left( \pi k \frac{m^*}{m_0} \right), \tag{6.14}$$

where

$$\psi(z) = \frac{z}{\sinh z}, \quad \lambda = 2\pi^2 \frac{T}{\hbar\omega_H}, \quad \omega_H = \frac{eH}{m^*c}.$$

In obtaining formula (6.14) we have used the fact that, in summing over the two spin directions [cf. (6.10)], everywhere except in the argument of the cosine one can replace  $\zeta_\sigma$  by  $\zeta$ , since  $\mu_0 H \ll \zeta$ . In the argument of the cosine one must expand  $S_m(\zeta_\sigma)$  in powers of  $\mu_0 H$  and stop at the first power of  $\mu_0 H$ . The inclusion of the small change in  $S_m$  is necessary here because, according to the condition  $cS/ehH \gg 1$ , even a small change in  $S_m$  causes a large change of the argument.

Formula (6.14) describes the main contribution to the oscillating part of the thermodynamic potential, i.e., it describes the oscillations with the largest amplitude. Analysis of (6.12) shows that oscillatory corrections appear because of singularities of  $S(\epsilon, p_z)$  or its derivatives. But for any nonconvex Fermi surface, over a large range of directions of the magnetic field there are singular sections of the figure-8 type, for which  $S(\zeta, p_z)$  has a singularity of the type  $\Delta p_z \ln \Delta p_z$ ,  $\Delta p_z = p_z - p_{zk}$ , where  $p_{zk}$  is the value of  $p_z$  corresponding to the singular section (cf. Sec. 3 of [1], and Secs. 2 and 3 of the Appendix). The integration near such a section gives a finite contribution to the oscillating part of the potential; according to [25], the amplitude of the oscillating terms due to "figure-

8's" is a factor of  $cS/ehH$  less than the amplitude of oscillations due to extremal sections.

Since  $\psi(z)$  is a monotonically decreasing function which is of the order of or less than unity [ $\psi(z) = 1$  for  $z = 0$ , and  $\psi(z) \approx 2ze^{-z}$  for  $z \gg 1$ ], while  $\partial^2 S/\partial p_z^2 \sim 1$ , at not too high temperatures the order of magnitude of  $\tilde{\Omega}$  is determined by the factor  $V/\hbar^3 (ehH/c)^{5/2} \cdot 1/m$ . For fields which are not too large ( $\mu H \ll \epsilon_F$ ), the monotonic part of the thermodynamic potential is of the order of its classical value, [23] i.e., of order  $(V/\hbar)^3 \int_0^\zeta \tau(\epsilon) d\epsilon$  (cf. formula (3.8')). If the

Fermi surface does not have an anomalously large anisotropy, the last expression is  $\sim V/\hbar^3 S^{5/2}/m$ . Thus the oscillating part of the potential is a small addition  $\sim (ehH/cS)^{5/2}$  to its regular (essentially classical) value. It follows therefore that the oscillatory part of the free energy  $\tilde{F}$  is numerically equal to  $\tilde{\Omega}$ , if we express the chemical potential  $\zeta$  in (6.14) in terms of the total number of electrons  $N$  and the volume  $V$ , i.e., if we replace  $\zeta$  by the Fermi energy  $\epsilon_F$ . There is of course a dependence of the chemical potential on magnetic field. It should lead to an oscillatory dependence of the thermionic emission current [26] (cf. also Sec. 8).

Thus formula (6.14) can be used directly to compute the observable quantities of interest. The oscillating part of the  $z$  component of the moment\* is  $M_z = -\partial\tilde{\Omega}/\partial H$ , while the corresponding part of the specific heat is  $\tilde{C} = -T \partial^2 \tilde{\Omega} / \partial T^2$ .

Formula (6.16) is valid for any arbitrary ratio of  $\hbar\omega_H = e\hbar H/m^*c$  and the temperature  $T$ . In deriving it we assumed only that  $T$  and  $\hbar\omega_H \ll \epsilon_F$ .

At absolute zero ( $T \ll \hbar\omega_H$ ), we have

$$\tilde{\Omega} \approx \frac{V}{2\pi^3 \sqrt{2\pi\hbar^3}} \left( \frac{e\hbar H}{c} \right)^{3/2} \sum_m \frac{1}{m^*} \left| \frac{\partial^2 S}{\partial p_z^2} \right|^{-1} \times \sum_{k=1}^\infty k^{-5/2} \cos \left\{ k \left( \frac{cS_m}{e\hbar H} - \pi \right) \pm \frac{\pi}{4} \right\} \cos \left( \pi k \frac{m^*}{m_0} \right). \tag{6.15}$$

At comparatively high temperatures ( $\lambda = 2\pi^2 \times (T/\hbar\omega_H) \gg 1$ ), only one of the terms in the summation over  $k$  is kept:

$$\tilde{\Omega} = \frac{V}{\hbar^3} \sqrt{\frac{2}{\pi^3}} T \left( \frac{e\hbar H}{c} \right)^{3/2} \sum_m \left| \frac{\partial^2 S}{\partial p_z^2} \right|_{\substack{\epsilon=\zeta \\ p_z=p_z^m}}^{-1/2} e^{-2\pi^2 T/\hbar\omega_H} \times \cos \left( \frac{cS_m}{e\hbar H} - \pi \pm \frac{\pi}{4} \right) \cos \left( \pi \frac{m^*}{m_0} \right). \tag{6.16}$$

Because of the factor  $2\pi^2$  in the condition for validity of formula (6.16), it is valid even at comparatively low temperatures† ( $T \gg \hbar\omega_H/20$ ).

\*In computing the  $x$  and  $y$  projections of the magnetic moment one must remember in the differentiation of  $\tilde{\Omega}$ , that  $m^*$  and  $S_m$  depend on the direction of the magnetic field.

†In making numerical estimates, one should remember that the effective mass  $m^*$  may differ substantially from the mass of a free electron.

According to formulas (6.14)–(6.16),  $\tilde{\Omega}$  is a complicated oscillatory function of the magnetic field, and the distance between zeros of this function (its “period”) is determined by the extremal sections of the Fermi surface:

$$\delta \frac{1}{H} = \frac{2\pi e\hbar}{cS_m} \quad (6.17)$$

It should be noted that if the dependence on the reciprocal of the field  $1/H$  is taken out of  $\tilde{\Omega}$ , the periods do not depend on the magnetic field. In addition  $\delta(1/H)$  is independent of the temperature.

If  $\delta H \ll H$ ,

$$\delta H = \frac{2\pi e\hbar}{cS_m} H^2, \quad (6.18)$$

i.e., at high fields the period is proportional to the square of the magnetic field.

The temperature dependence of  $\tilde{\Omega}$  is determined by the value of the effective mass  $m^*(\epsilon_F, p_{zm})$ . But one should remember that interactions of the electrons with impurities, with lattice vibrations and with other disturbances in the periodicity of the crystal lead to a reduction in the amplitude of oscillation.\* Inclusion of the scattering on impurities (Bychkov<sup>[27]</sup>) shows that the effect of reduction of the oscillation amplitude can be taken into account by replacing the temperature by an effective temperature  $T + \hbar/\tau$ , where  $\tau$  is of the order of the mean free time for the electron (qualitatively this result had been obtained by Dingle<sup>[28]</sup>). The formulas of Dingle and Bychkov, which were derived assuming a quadratic dispersion law for the conduction electrons, are convenient for estimates of the amplitude.†

We shall now find the expression for the component of the magnetic moment along the magnetic field. Since  $cS_m/e\hbar H \gg 1$ , we need only differentiate the cosine, and not the slowly varying amplitude:

$$\begin{aligned} \tilde{M}_z \approx & -\frac{V}{\hbar^3} \frac{1}{2\pi^3} \frac{1}{2\pi} \left(\frac{e\hbar}{c}\right)^{3/2} \sqrt{H} \sum_m \frac{S_m(\epsilon_F)}{m^* \left| \frac{\partial^2 S}{\partial p_z^2} \right|^{1/2}} \\ & \times \sum_{k=1}^{\infty} \frac{\Psi(k\lambda)}{k^{3/2}} \sin \left[ k \left( \frac{cS_m}{e\hbar H} \right) - \pi \right] \pm \frac{\pi}{4} \cos \left( \pi k \frac{m^*}{m_0} \right). \end{aligned} \quad (6.19)$$

In relatively large fields at low temperatures, i.e., for  $\psi \approx 1$ , the oscillating part of the moment is considerably greater than its monotonic part. In fact one can show that  $M \sim (V/\hbar^3)(e\hbar/c)^2(S^{1/2}H/m^*)$ , i.e.,  $\tilde{M}/M \sim (cS/e\hbar H)^{1/2} \gg 1$ .

For the estimate, we started from the expression for  $M$  given in the paper of Lifshitz and Kosevich [cf. formula (A.2) of <sup>[22]</sup>].

\*The next section discusses the electronic interaction.

†We should mention that the qualitative treatment (Dingle<sup>[24]</sup>) does not enable one to include the influence of collisions on the oscillational effects. In particular, the value of  $\partial M_z/\partial H$  computed by Bychkov<sup>[27]</sup> differs considerably from that given by Dingle’s formulas.<sup>[24]</sup>

The fact that the oscillating part of the moment turned out to be considerably larger than its monotonic part should not be surprising, since the whole moment (including the monotonic part) is of quantum mechanical origin.

The relatively large values of  $\tilde{M}$  makes the observation of the oscillatory effects easier.

Figure 15 shows typical curves for the magnetic moment as a function of magnetic field. In most metals the dependence of the magnetic moment on magnetic field is not limited to a single harmonic, but is a superposition of several harmonics which, as a rule, have markedly different periods (Fig. 16). This means that for most metals the Fermi surface is very complicated, and the numerical estimates show that for all

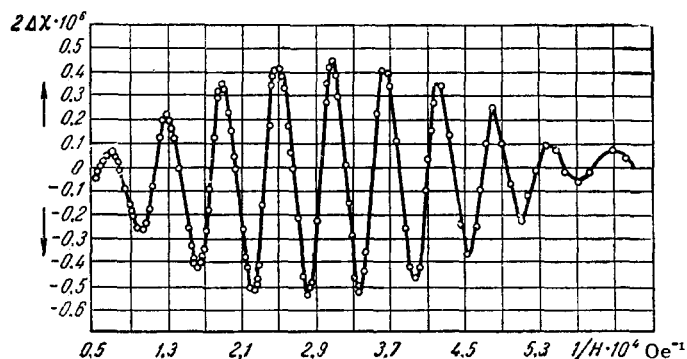


FIG. 15. Typical curve of dependence of magnetic susceptibility on inverse magnetic field (Zn,  $T = 4.2^\circ \text{K}$ <sup>[48]</sup>).

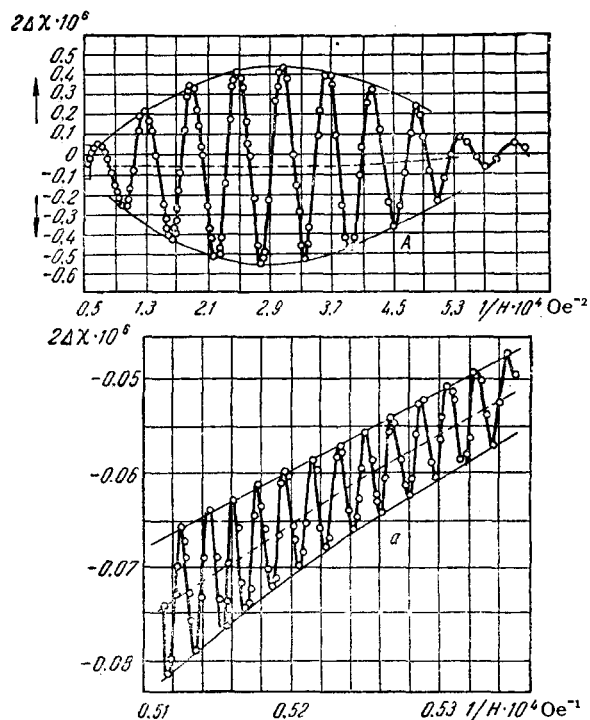


FIG. 16. Fine structure of the de Haas–van Alphen effect in a Zn crystal ( $T = 4.2^\circ \text{K}$ ). Curve *a* is an enlargement along both axes of the portion of the main curve *A* which is contained in the rectangle in the upper figure.

metals except those of the first group there are relatively small sections, whose size is considerably smaller than  $(h/a)^2$ , where  $a$  is the lattice constant ( $S_0 = 4\pi(3/8\pi)^{2/3}(2\pi\hbar)^2/a^2$  is the maximum cross section of the Fermi sphere for a free electron gas with density equal to  $1/a^3$ ). Usually in deciphering the experimental data one assumes that small sections correspond to the existence of isolated small sheets of the Fermi surface.\* An estimate of the volume of such sheets show that they may contain  $\sim 10^{-5}$  electrons (or "holes") per atom. An estimate of the amplitude, i.e., the factor in front of the cosine, leads to extremely small values of the effective masses of the electrons located on the small sections ( $m^* \sim (10^{-3}-10^{-2})m_0$ , where  $m_0$  is the free electron mass).

The large number of extremal sections, i.e., the large number of harmonics in the dependence of the magnetic moment on magnetic field, makes it very difficult to decipher the experimental curves. But the use of different ranges of fields and the careful measurement of the angular dependence of the periods (cf., for example, Fig. 17) has made it possible not only to unravel the  $\tilde{M}(H)$  curves but to determine the shape of the Fermi surface of several metals from measurements of the periods (cf. Sec. 9).

Let us consider still another phenomenon, which has been called "magnetic breakdown."<sup>[29]</sup> During the motion of an electron along the quasiclassical trajectory, there is usually a very small probability for it to make a transition to a neighboring trajectory. But if the trajectories are close, in sufficiently high fields the electron, which doesn't "notice" the low potential barriers between the trajectories, will move along a "trajectory" which consists of pieces of several different trajectories (Fig. 18). In this case there may be periods among the harmonics of the

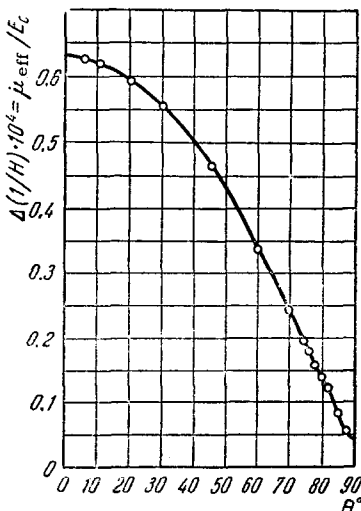


FIG. 17. Dependence of period of oscillation on direction of magnetic field.

\*According to <sup>[25]</sup> the existence of small sections is related not only to the sheets that split off, but also to small bumps and dimples on the Fermi surface.

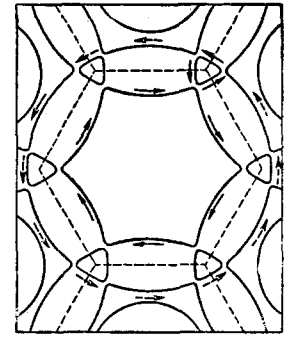


FIG. 18. "Magnetic breakdown." The solid arrows show the trajectory of an electron when the field is not too large; the dashed arrows show the path in a high field; the dashed lines are the boundary of the Brillouin zone.

de Haas-van Alphen effect to which there correspond areas exceeding the size of the section of the Brillouin zone even for metals with a closed Fermi surface. This apparently has been seen by Priestley in magnesium.<sup>[29]</sup>

The distances between classical trajectories are very small if these trajectories pass near a point where the degeneracy is lifted by any small interaction (for example, by spin-orbit interaction). It is easy to estimate the fields at which one should observe magnetic breakdown: the distance between levels should be considerably larger than the energy of the interaction which lifts the degeneracy.

## 7. THE DE HAAS-VAN ALPHEN EFFECT AND THE THEORY OF THE FERMI LIQUID

As we have already stated, most of the results found in the preceding sections are "stable" to a change from the Fermi gas to a Fermi liquid. But the dispersion law for the elementary excitations, which we shall be considering, naturally includes the interaction between electrons. This is in the spirit of the Landau theory of the Fermi liquid. According to <sup>[2]</sup>, the basis for the construction of the spectrum of the Fermi liquid type is the assumption that as the interaction between electrons is gradually "switched on," i.e., as we go from the gas to the liquid, the classification of the levels remains unchanged—the state of the "electron" can still be described by giving the zone number  $s$  and the quasimomentum  $p$ , provided the metal does not go over into the superconducting state. In this classification, the role of the gas particles is taken over by the elementary excitations (quasiparticles), each of which has a definite momentum. They obey Fermi statistics, and their number is always equal to the number of particles in the liquid. In a certain sense the quasiparticle can be regarded as a particle which is in the self-consistent field of the surrounding particles. Naturally then the energy of the particle depends on the state of the surrounding particles, and the energy of the system is not the sum of the individual energies of the particles of the system but is a functional of the distribution function. This last statement is the basic idea of the theory of the Fermi liquid.

The possibility of introducing quasiparticles with a definite momentum (or quasimomentum) is supported by the fact that the probability of collision for a particle which is within the region of smearing of the Fermi surface is proportional not only to the interaction strength but also to the square of the temperature. Thus the small parameter with which the theory of the Fermi liquid is built up is not the interaction between electrons, but rather any quantity characterizing the deviation of the distribution function from the Fermi step function, for example, the temperature (or, to be more precise,  $T/\epsilon_F$ ).

If we consider only small deviations from the Fermi step function, the energy of the system can be written as an expansion in powers of the deviation  $\nu(\mathbf{p})$  of the distribution from  $n_0(\epsilon)$ :

$$E = E_0 + \int \epsilon \nu(\mathbf{p}) d\tau_{\mathbf{p}} + \frac{1}{2} \int \int f(\mathbf{p}, \mathbf{p}') \nu(\mathbf{p}') \nu(\mathbf{p}) d\tau_{\mathbf{p}'} d\tau_{\mathbf{p}},$$

$$d\tau_{\mathbf{p}} = \frac{2}{(2\pi\hbar)^3} dp_x dp_y dp_z. \quad (7.1)$$

Here  $E_0$  is the ground state energy (for  $\delta n \equiv 0$ ),  $\epsilon = \delta E/\delta \nu$  is the change in energy of the system when the number of particles in the system changes by unity, i.e., the energy of a quasiparticle, while  $f(\mathbf{p}, \mathbf{p}') = \delta^2 E/\delta \nu(\mathbf{p}) \delta \nu(\mathbf{p}')$  is the correlation function, the main quantity characterizing the interaction between particles in Landau's theory of the Fermi liquid.<sup>[2]</sup> For simplicity we shall not take account of the electron spin.

The formulas derived in the preceding section were obtained neglecting interaction. Including collisions of electrons with impurities and with phonons shows that making the electron mean free path finite does not change the oscillation periods but reduces the oscillation amplitudes. The interactions of electrons among themselves have a more complicated effect. First of all, electron collisions, which are responsible for the electronic part of the resistance, reduce somewhat the amplitude of the oscillations. Second, as we have stated, the interaction between electrons in the spirit of the theory of the Fermi liquid enters into the dispersion law for the quasiparticles (which we have been calling conduction electrons). It is just this dispersion law, which includes the interaction between electrons, which enters in the quantization condition (6.8) and, consequently, determines the periods of oscillation. We should point out that the interaction between electrons enters in the periods only through the dispersion law. To prove this last statement, we show that the distance between interacting conduction electrons in a magnetic field (in the quasiclassical approximation) is determined as before by the familiar formula\*

\*In order for the results of the "gas" and "liquid" treatments to coincide, not only must their spectra be the same but also the density of states. The fact that the density of states for a Fermi liquid is the same as for a Fermi gas will be proved at the same time as formula (7.2).

$$\Delta \epsilon = \hbar \omega_H, \quad \omega_H = \frac{eH}{m^*c}, \quad m^* = \frac{1}{2\pi} \frac{\partial S}{\partial \epsilon}. \quad (7.2)$$

We emphasize once more: the proof of formula (7.2) does not mean that the interaction between electrons "drops out" of the quantization condition. It means that the interaction appears in the quantization condition only through the dispersion law  $\epsilon = \epsilon(\mathbf{p})$  which, as we have said, includes the interaction.

To prove (7.2) we use the fact that, in the quasiclassical approximation,

$$\epsilon_{n+1} - \epsilon_n = \Delta \epsilon = \hbar \omega, \quad (7.3)$$

where  $\omega$  is the frequency of the classical motion. Thus we must find the frequency of the classical motion of the electron in a magnetic field. To do this we consider the vibrations of the electron liquid in a magnetic field.

The state of the electrons is described by a distribution function  $n(\mathbf{r}, \mathbf{p}; t)$ , which satisfies the kinetic equation

$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial \mathbf{r}} \mathbf{v} + \frac{\partial n}{\partial \mathbf{p}} \mathbf{F} = 0. \quad (7.4)$$

Here  $\mathbf{v}$  is the particle velocity

$$\mathbf{v} = \frac{\partial \epsilon}{\partial \mathbf{p}} + \frac{\partial}{\partial \mathbf{p}} \int f(\mathbf{p}, \mathbf{p}') \nu(\mathbf{p}') d\tau_{\mathbf{p}'}$$

In the case which we are treating, the force acting on the electron is the Lorentz force

$$\mathbf{F} = \frac{e}{c} [\mathbf{v}, \mathbf{H}]. \quad (7.5)^*$$

Linearizing Eq. (7.3) and making use of the spatial homogeneity of the problem, we easily find

$$\frac{\partial \mathbf{v}}{\partial t} + \frac{e}{c} [\mathbf{v}_0, \mathbf{H}] \frac{\partial \mathbf{v}}{\partial \mathbf{p}} = - \frac{\partial n_0}{\partial \epsilon} \frac{e}{c} \int \mathbf{v}_0 \left[ \frac{\partial}{\partial \mathbf{p}} f(\mathbf{p}, \mathbf{p}') \nu(\mathbf{p}'), \mathbf{H} \right] d\tau_{\mathbf{p}'}, \quad (7.6)$$

where  $\mathbf{v}_0 = \partial \epsilon / \partial \mathbf{p}$  is the velocity of the particle for  $\nu \equiv 0$  ( $\nu(\mathbf{p}) = n(\mathbf{p}) - n_0(\epsilon)$ ).

If we introduce a new function  $\chi$  ( $\nu = -(\partial n_0 / \partial \epsilon) \chi$ ) and change from the variables  $p_x, p_y, p_z$  to the variables  $\epsilon, \tau, p_z$ , where  $\tau$  is the time for traversing the quasiclassical trajectory, the kinetic equation (7.6) can easily be written in the following form:†

$$\frac{\partial \chi}{\partial t} + \frac{\partial \chi}{\partial \tau} = \int F(p_z, \tau; p'_z, \tau') \chi(p'_z, \tau') dp'_z d\tau'. \quad (7.7)$$

The expression for the function  $F(p_z, \tau; p'_z, \tau')$  is determined by comparing with the integral part of Eq. (7.6). The integration in (7.6) goes over the Fermi surface, since  $\partial n_0 / \partial \epsilon = -\delta(\epsilon - \epsilon_F)$ . The solution of Eq. (7.6) is assumed to have the following form:

$$*[\mathbf{v}, \mathbf{H}] = \mathbf{v} \times \mathbf{H}.$$

†The reason why the left side of the kinetic equation is so simple when one uses the variables  $p_z, \epsilon$  and  $\tau$  is that  $p_z$  and  $\epsilon$  are conserved in a constant, homogeneous magnetic field, and  $\tau$  is canonically conjugate to  $\epsilon$ .

$$\chi(p_z, \tau; t) = ie^{-i\omega t} \sum_n \chi_n(p_z) e^{in\omega_H(p_z)\tau}, \quad (7.8)$$

which is justified because of the periodic dependence of the distribution function on  $\tau$  (we are, of course, considering closed sections on the Fermi surface).

Substituting the expansion (7.8) in Eq. (7.7), we get

$$[\omega - n\omega_H(p_z)] \chi_n(p_z) = \sum_{n'} \int F_{nn'}(p_z, p'_z) \chi_{n'}(p'_z) dp'_z \quad (7.9)$$

(we shall not give the relation between  $F$  and  $F_{nn'}$ ). For simplicity we shall suppose that the operator  $F_{nn'}$  is degenerate, i.e., we shall assume that

$$F_{nn'} = \delta_{nn'} g_n(p_z) g_n^*(p'_z). \quad (7.10)$$

From the rest of the derivation it will be clear that this simplifying assumption does not spoil the main result. From (7.10) and (7.9) we get

$$[\omega - n\omega_H(p_z)] \chi_n(p_z) = g_n(p_z) \langle \chi_n, g_n \rangle, \quad (7.11)$$

where

$$\langle \chi_n, g_n \rangle \equiv \int \chi_n(p'_z) g_n^*(p'_z) dp'_z \quad (7.12)$$

is the scalar product of the functions  $g_n(p_z)$  and  $\chi_n(p_z)$ . Since we are interested in the distance between neighboring levels, we consider the case of  $n = 1$ :

$$[\omega - \omega_H(p_z)] \chi_1(p_z) = g_1 \langle \chi_1, g_1 \rangle.$$

From the last equation we have  $\langle \chi_1, g_1 \rangle = \int \frac{g_1^2 dp_z}{\omega - \omega_H(p_z)} \langle \chi_1, g_1 \rangle$ , so that the dispersion equation for determining the vibration frequencies  $\omega$  is written as follows:

$$1 = \int \frac{|g_1|^2 dp_z}{\omega - \omega_H(p_z)}. \quad (7.13)$$

To analyze this equation it is convenient to change from continuous to discrete values of the momentum, for example, by introducing a quantization of the momentum due to the boundaries of the metal. Then Eq. (7.13) takes the form

$$1 = \sum \frac{|g_1|^2 \Delta p_z}{\omega - \omega_H(p_z)}, \quad (7.14)$$

in which  $p_z$  takes on a discrete set of values  $p_z^{(k)}$ . Figure 19 shows the graphical solution of (7.14), and we see that the roots are located between the values  $\omega_H(p_z^{(k)})$ . Furthermore there is one root which has been sloughed off (Fig. 19). When we "go back" to the continuous spectrum (say, by letting the dimensions of the sample go to infinity), the vibration frequencies tend toward the values  $\omega_H(p_z)$ . In addition there is one frequency which is pushed out and corresponds to zero sound in the Fermi liquid.<sup>[30]</sup> Since the frequencies are rigorously required to be between the values  $\omega_H(p_z^{(k)})$ , it is clear that the spectral density (the number frequencies in the range  $(p_z, p_z + dp_z)$  for a Fermi liquid is the same as for a Fermi gas.

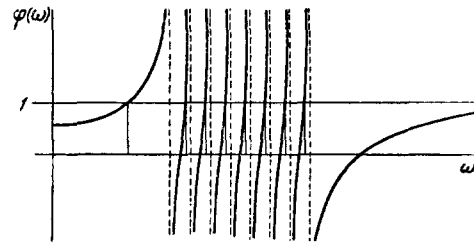


FIG. 19. Graphical solution of the dispersion equation (7.14).

$$\varphi(\omega) = 1, \quad \varphi(\omega) = \sum \frac{|g_1|^2 \Delta p_z}{\omega - \omega_H(p_z)}.$$

We note that for a quadratic dispersion law,  $\omega_H$  is independent of  $p_z$ . The vibration frequency is of course equal to  $eH/mc$ .

Thus formula (7.1) determines the quasiclassical quantization of the energy levels of a Fermi liquid in a magnetic field. We have thus shown that the formulas of the preceding section (the oscillation periods) are valid not only for a Fermi gas but also for a Fermi liquid, if we understand  $\epsilon(p)$  to be the dispersion law including the interaction between electrons in the ground state.\*

## 8. THE DE HAAS-VAN ALPHEN EFFECT (SPECIAL PROBLEMS)

We shall discuss some special problems concerning the theory of the de Haas-van Alphen effect.

In<sup>[31]</sup>, the de Haas-van Alphen effect in thin metallic layers was treated. The starting assumption of this work was the picture of the metal as a potential well. Using this assumption, the quasiclassical energy levels of the conduction electron were calculated [cf. (5.16)–(5.22) in<sup>[1]</sup>] and the dependence of the oscillating part of the magnetic moment on the magnetic field and the film dimensions were studied. In particular it was shown that the period of oscillations in the film parallel to the magnetic field is the same as the period of the bulk metal if the electron orbit corresponding to the extremal area of section of the Fermi surface lies within the film (first curve of Fig. 11 in<sup>[1]</sup>). If the "extremal" orbit is not located inside the film (second curve of Fig. 11), the period of  $\tilde{\Omega}$  (and  $\tilde{M}$ ) is determined by the area bounded by the trajectory of the electron in momentum space and the straight lines  $P_x = p_x + eH/cd$ , where  $d$  is the half-thickness of the film, the  $z$  axis is as always along the magnetic field, and the  $y$  axis is perpendicular to the surface of the film. In this case the period depends on the dimensions of the film and on the magnetic field.

The picture given here of the dependence of the oscillatory effects on film dimensions is valid, as we have

\*The proof given here was first found by I. M. Lifshitz (1957). Recently this result has been confirmed by direct calculation in a paper of Bychkov and Gor'kov.<sup>[15]</sup>

said, only if the walls of the metal can be regarded as an infinitely high potential barrier. In other words, it is assumed in [31] that there is specular reflection of electrons from the boundary. Actually the scattering of electrons seems to be almost diffuse. This means that when it collides with the boundary an electron "forgets" its motion before the collision. In particular, the reflection condition is formulated not for an individual electron but for the electron distribution function. [32]

If there is diffuse scattering of the electrons from the metal boundary, the nature of the dependence of the oscillatory part of the magnetic moment on magnetic field and on film dimensions is different. If the extremal orbit is located within the film, the oscillation period in the film is again the same as for the bulk metal. But if the trajectory is not located within the film, the corresponding harmonic in the oscillatory dependence of the magnetic moment on magnetic field has a much smaller amplitude (M. Azbel' [33]). This fact provides another possibility for determining the shape of the Fermi surface from the experimental data (Sec. 9).

As we have already pointed out, the experimentally observed dependence of the magnetic moment on magnetic field is very complicated, and in many metals the  $M = M(H)$  curves contain harmonics corresponding to very small periods. To "resolve" them one uses high magnetic fields ( $\sim 10^5$  Oe), since according to (6.18) the period is proportional to the square of the magnetic field. High magnetic fields are obtained most often at present by using pulse techniques. Because of the skin effect, the electrons are then located in an inhomogeneous magnetic field. An analysis of the effect of inhomogeneity (A. Kosevich [34,35]) shows that in order to interpret the experimental data, i.e., to relate the observed periods to extremal sections of the Fermi surface, requires that several conditions be satisfied.\*

Let  $L$  be the characteristic dimension of the sample (film thickness, for example),  $T_0$  the characteristic time of variation of the magnetic field,  $\delta$  the skin depth ( $\delta \sim \sqrt{c^2 T_0 \rho}$ , where  $\rho$  is the resistivity of the sample in the maximum magnetic field  $H_m$ ). Then the conditions mentioned can be written as follows: [34] either

$$\omega_H T_0 \gg \frac{\delta}{a} \gg \frac{L}{a} > \frac{r_m}{a}, \quad (8.1)$$

or

$$L \gg \delta \gg r_m, \text{ and } \omega_H T_0 \gg \frac{\delta}{a}. \quad (8.1')$$

\*The oscillation amplitude when one applies a pulsed field is naturally less than for a steady field. But the use of experimental techniques in which one measures not  $M(H)$ , but  $dM/dH$ , makes it easier to observe the effect, since differentiation is equivalent to multiplying by the factor  $cS_m/e\hbar H$ , which is considerably greater than unity.

Here  $a$  is the interatomic spacing and  $r_m$  is the radius of the electron orbit in the field  $H_m$ . We note that in [36,37], which used pulse methods to detect and study oscillations of the magnetic susceptibility of many metals of the first group of the periodic table, condition (8.1) was satisfied.

We have stated repeatedly that oscillation effects which owe their origin to oscillations of the density of electron states may manifest themselves not only in an oscillatory dependence of the magnetic moment on magnetic field but also in a dependence of thermodynamic and kinetic quantities on the magnetic field. In fact oscillations of resistivity, Hall field, thermal conductivity and thermomagnetic characteristics of various metals have been seen experimentally. The theory of the kinetic properties of metals in a magnetic field will be presented in the third part of this survey.

Here we shall only point out some possibilities for observing oscillations of the contact potential difference [26] and the tunnel current. [38]

The contact difference of potential  $\delta\varphi$  between two samples, of which one is in a magnetic field, aside from a term related to the difference in state of the surface of the samples, is given by the difference in their chemical potentials

$$e\delta\varphi = \zeta(H) - \zeta(0). \quad (8.2)$$

According to [26] this difference is equal to

$$e\delta\varphi = \frac{2\sqrt{2\pi}}{v(\epsilon_F)} \left( \frac{c\hbar H}{c} \right)^{3/2} \sum_m \left| \frac{\partial^2 S_m}{\partial p_z^2} \right|^{-1/2} \times \sum_k \frac{\psi(k\lambda)}{k^{3/2}} \sin \left\{ k \left( \frac{cS_m}{e\hbar H} - \pi \right) \pm \frac{\pi}{4} \right\} \cos \left( \pi k \frac{m^*}{m_0} \right) \quad (8.3)$$

(the notation is the same as in Sec. 6). Numerical estimates show that the amplitude of the oscillations of the contact potential difference is of the order of, or somewhat greater than,  $10^{-6}$  V [provided, of course, that the temperature is sufficiently low ( $\hbar\omega_H \gtrsim T$ )].

A tunnel diode consists of two metals separated by a thin ( $\sim 10^{-7}$ – $10^{-6}$  cm) dielectric layer; it has been used successfully to determine the size of the energy gap in superconductors. V. Bar'yakhtar and V. Makarov [38] have suggested using such equipment for simultaneous measurement of the extremal sections and the corresponding effective masses.

A calculation of the tunnel current  $j$ , for a difference of potential  $\varphi$ , in a magnetic field perpendicular to the separating film, gives the following result:

$$\tilde{j} = \sum_m \sum_{k=1}^{\infty} A_m(k) \sin \left\{ k \left( \frac{cS_m}{e\hbar H} - \pi \frac{e\varphi}{\hbar\omega_H} \right) \pm \beta_m \right\} \sin \left( \pi \frac{e\varphi}{\hbar\omega_H} k \right). \quad (8.4)$$

The summation in (8.4) extends over all extremal sections of the Fermi surface for which  $v_z \geq 0$ :

$$A_m(k) = -\frac{e}{4\pi^3 n} \left( \frac{eH}{ck} \right)^2 \left\{ \frac{\partial S}{\partial \epsilon} \frac{\partial v_z}{\partial p_z} D \right. \\ \left. \frac{\partial S}{\partial \epsilon} \frac{\partial^2 S}{\partial p_z^2} \right\} \Psi(k\lambda) \Big|_{p_z = p_{zm}} \quad (8.5)$$

and

$$\beta_m = -\pi \pm \frac{\pi}{2}. \quad (8.6)$$

The plus sign in (8.6) is used if the extremal section is a minimum, and the minus sign if it is a maximum.

We see from (8.4) that the tunnel current oscillates not only when a magnetic field is applied (the periods of these oscillations are the same as for the de Haas-van Alphen effect, but the number of harmonics is less, since the harmonics with  $v_z < 0$  drop out), but also when the applied voltage  $\varphi$  is changed; the period of the  $\varphi$  oscillations is determined by the effective masses associated with the extremal sections. According to the numerical estimates, the amplitude of oscillations of the tunnel current is  $\hat{j} \gtrsim 10^{-6} j_0$ , where  $j_0$  is the monotonic part of the current passing through the tunnel diode.

## 9. DETERMINATION OF THE ELECTRON ENERGY SPECTRUM FROM EXPERIMENTAL DATA\*

A great variety of methods are used at present for determining the energy spectrum of condensed systems (ultrasonic absorption, galvanomagnetic phenomena, anomalous skin effect, de Haas-van Alphen effect, inelastic scattering of neutrons, characteristic energy losses of electrons, etc).

If we are dealing with the determination of Bose branches of the spectrum, the methods which are most promising and which give the most complete information are those based on the interaction of penetrating particles with a known energy spectrum (neutrons, relatively energetic electrons, photons) with the elementary excitations which are being studied. When conditions analogous to those for Cerenkov radiation are satisfied, the penetrating particle excites a single elementary excitation (it "creates" a boson and with energy  $\epsilon$  quasimomentum, or momentum,  $p$ ). Thus a study of the inelastic scattering of the particles (neutrons, etc) can completely determine the dispersion law  $\epsilon(p)$  for the elementary excitations. This method has been used successfully to determine experimentally the phonon-rotor spectrum in He II, the phonon spectra of many solids (from inelastic scattering of neutrons), the plasma oscillations of electrons in a metal (from the spectrum of characteristic energy losses of electrons passing through thin films) etc.

To compute the thermodynamic characteristics, it is sufficient to know the level density  $\nu(\epsilon)$ , which in the case of Bose branches of the spectrum can be determined in principle from the temperature dependence

of the specific heat and other thermodynamic quantities.<sup>[40]</sup> But this method is not very stable and therefore requires tremendous accuracy of the experimental data.

Now let us look at the Fermi branches of the spectrum. As we have often said, one can speak of a one-electron spectrum (in the fermion sense) only when the "electron" or "hole" is near the Fermi surface. Thus the problem of establishing the electron energy spectrum (or the electronic dynamic structure of the metal) is very much restricted in scope—one must determine the shape of constant-energy surfaces located near the Fermi surface. Since the electron velocity is  $v = \partial\epsilon/\partial p$ , it is sufficient to determine the shape of the Fermi surface and the distribution of velocities on it. As for the energies which are far from the limiting surface  $\epsilon_F$ , here one can apparently only pose the question of determining the density of electron states per unit energy range  $\nu(\epsilon)$ . The latter quantity can be gotten from x-ray absorption spectra. Furthermore, the suggestion has been made<sup>[41]</sup> to use the  $\gamma$  quanta from positron absorption in metals to probe the deep electron energy levels.

As investigations in recent years have shown, there are a large number of phenomena which are sensitive to anisotropy of the dispersion law for conduction electrons (the anomalous skin effect, the de Haas-van Alphen effect, cyclotron resonance, ultrasonic absorption in a magnetic field, etc). They all give some information about the electron energy spectrum. One can achieve a complete unravelling of the electron dynamic structure only by using many different methods. The best developed methods are those for determining the electron spectrum using measurements in relatively high magnetic fields\* (the de Haas-van Alphen effect, cyclotron resonance, absorption of ultrasound in a magnetic field, galvanomagnetic phenomena).

In this section we discuss the possibility of determining the electron energy spectrum from observations of the de Haas-van Alphen effect. We start from the main oscillatory terms in the magnetic moment, i.e., from those terms which are due to the extremal sections of the Fermi surface (cf. Sec. 6). The starting expression is (6.19), which shows that the dependence of the period of each harmonic  $\Delta(1/H)$  on the direction of the magnetic field determines the dependence on angle of the area of the extremal sections  $S_m$ . Measurement of the amplitude of harmonics and their temperature dependence makes it possible to determine the derivative  $\partial S_m / \partial \xi = 2\pi m^*(\xi, p_{zm})$ . However, for the determination of the effective mass one must bear in mind the remarks in Secs. 6 and 7 about the effect of interaction on the amplitude of oscillation.

\*The problems of determining the electron energy spectrum of metals from experimental data are discussed in a detailed survey by A. Pippard.<sup>[39]</sup>

\*For all these methods it is necessary that the condition  $\omega_H \tau \gg 1$  be satisfied; this condition means that the electrons go through a sufficient number of revolutions in the magnetic field in the time between collisions ( $\tau$  is the mean free time).

Since even when the interaction is taken into account the amplitude of the oscillations is expressed in terms of the dispersion law (cf. Sec. 7), while the amplitude is not, it is obvious that the de Haas-van Alphen effect is extremely convenient for determining the shape of the Fermi surface, but gives considerably less satisfactory data regarding the distribution of velocities on the Fermi surface (for the relation between the effective mass and the velocity  $\mathbf{v} = \partial\epsilon/\partial\mathbf{p}$ , cf. below).

Let  $\xi$  be a unit vector along the magnetic field, and  $\sigma(\xi) = [S_m(\zeta)]_\xi$  be the extremal area of the section of the Fermi surface  $\epsilon(\mathbf{p}) = \zeta$  by a plane perpendicular to  $\xi$ . Then, according to (6.19),

$$\sigma(\xi) = \frac{2\pi\epsilon\hbar}{c\Delta_\xi}, \quad (9.1)$$

where  $\Delta_\xi$  is the period (in units of the reciprocal field) of the corresponding harmonic of the oscillation.

It is assumed that the Fermi surface has a center of symmetry and that every ray drawn from the center meets the surface at only one point. If the Fermi surface breaks up into several closed surfaces, the following considerations apply to each of them.

For surfaces having this property, the extremal section is central. We denote the length of the radius vector drawn from the center of the surface in the direction  $\mathbf{e}$  by  $\rho(\mathbf{e})$ . Then

$$\sigma(\xi) = \frac{1}{2} \int \rho^2(\mathbf{e}) \delta(\mathbf{e}\xi) d\Omega_\xi, \quad (9.2)$$

where  $\delta(x)$  is the Dirac  $\delta$ -function,  $d\Omega_\xi$  is the element of area of the unit sphere. In other words,

$$\sigma(\xi) = \pi \overline{\rho^2(\mathbf{e})} |_{\mathbf{e}\xi=0}, \quad (9.3)$$

i.e.,  $\sigma(\xi)$  is the mean square of the radius vector  $\rho(\mathbf{e})$  on the equator which is defined by  $(\mathbf{e}\cdot\xi) = 0$ .

Thus construction of the surface reduces to determining the function  $\pi\rho^2(\mathbf{e})$  (where  $\rho(-\mathbf{e}) = \rho(\mathbf{e})$ ) from its average values on the equator  $\mathbf{e}\cdot\xi = 0$  for arbitrary  $\xi$ .

The solution of this problem can be gotten from the following relations, which can be easily shown by direct computation to be valid for an arbitrary function  $\psi(\xi) = \psi(-\xi)$ , given on the unit sphere:

$$\int \bar{\psi}(\xi) d\Omega - \int_{z^2 > \lambda^2} \frac{\bar{\psi}(\xi) z}{\sqrt{z^2 - \lambda^2}} d\Omega = \int_{z^2 > 1 - \lambda^2} \psi(\xi) d\Omega, \quad (9.4)$$

$$z = (\mathbf{e}\xi), \quad \lambda^2 < 1.$$

Here  $\bar{\psi}(\xi)$  denotes the average value of the function  $\psi(\mathbf{e})$  on the equator  $\mathbf{e}\cdot\xi = 0$ ; the region of integration on the surface of the unit sphere is determined by the inequalities.

Setting  $\psi(\xi) = \pi\rho^2(\xi)$ ,  $\bar{\psi}(\xi) = \sigma(\xi)$ , we have for sufficiently small  $\lambda$ ,

$$\pi\rho^2(\mathbf{e}) = \left\{ \int \sigma(\xi) d\Omega - \int_{z^2 > \lambda^2} \frac{\sigma(\xi) z}{\sqrt{z^2 - \lambda^2}} d\Omega \right\} / \pi\lambda^2, \quad z = \xi\mathbf{e}. \quad (9.5)$$

Going to the limit  $\lambda \rightarrow 0$ , we get

$$\pi\rho^2(\mathbf{e}) = \chi_e(0) - \int_0^1 [\chi_e(u) - \chi_e(0)] \frac{du}{u^2},$$

$$\chi_e(u) = \overline{\sigma(\xi)} |_{\xi\mathbf{e}=z} = \frac{1}{2\pi} \int \sigma(\xi) \delta(\xi\mathbf{e} - u) d\Omega_\xi. \quad (9.6)$$

If in each case we choose the direction of  $\mathbf{e}$  as the polar axis of our coordinate system and introduce the angle through the equation  $\cos \theta = \xi \cdot \mathbf{e}$ , and also use the polar angle  $\varphi$  in the plane perpendicular to  $\mathbf{e}$ , we can, writing  $\sigma(\xi)$  as  $\sigma_\mathbf{e}(\cos \theta, \varphi)$ , integrate by parts and write the expression in the form

$$\pi\rho^2(\mathbf{e}) = \sigma(\mathbf{e}) - \frac{1}{2\pi} \int_0^{2\pi} d\varphi \int_0^1 \frac{\partial \sigma_\mathbf{e}(\cos \theta, \varphi)}{\partial \cos \theta} \frac{d \cos \theta}{\cos \theta}. \quad (9.6a)$$

Formula (9.6) solves our problem; for numerical computations it is apparently more convenient to use formula (9.5) with some value of  $\lambda \ll 1$ .

As we see from (9.6), the solution is stable; the mean error in determining the shape of the surface is related to the error in determining the area  $\sigma(\xi)$  [i.e., the period  $\delta(1/H)$ ]. In order of magnitude,  $\delta\rho^2 \sim \delta\sigma$ .

In reproducing the shape of the surface, we get at the same time the value of  $\partial^2 S(\zeta, p_z) / \partial p_z^2$ , which is thus not an independent parameter. An additional parameter is the quantity  $\partial S_m / \partial \zeta$ , which can be determined from measuring the oscillation amplitudes or their temperature dependence. Knowing the value of  $\partial S_m / \partial \zeta$  as a function of the magnetic field direction  $\xi$ , we can determine the velocity of the electrons on the limiting surface.

The velocity  $\mathbf{v}$  is given by  $\mathbf{v} = \partial\epsilon/\partial\mathbf{p}$ . If in addition to the surface  $\epsilon(\mathbf{p}) = \zeta$ , we consider the neighboring surface  $\epsilon(\mathbf{p}) = \zeta + d\zeta$ , then

$$v = |\nabla\epsilon| = \frac{\delta\zeta}{\delta n},$$

where  $\delta n$  denotes the distance between the surfaces along the normal. On the other hand, the neighboring surface will have an extremal section area equal to

$$S_m(\zeta + \delta\zeta) = S_m(\zeta) + \delta\zeta \frac{\partial S_m}{\partial \zeta}.$$

For the surfaces we are considering, the extremal section coincides with the central section ( $p_z = 0$ ). Thus the derivative with respect to the chemical potential is taken at constant  $p_z$ , i.e.,  $\partial S_m / \partial \zeta = 2\pi m^*$ , or in the notation used before,

$$\delta\sigma(\xi) = \delta\zeta \frac{\partial S_m}{\partial \zeta} \Big|_\xi.$$

According to (9.6), this enables one to determine  $\delta\rho^2(\mathbf{e})$  and consequently  $\delta n = \delta\rho(\mathbf{e}\cdot\mathbf{n})$ . This solves our problem:

$$\frac{1}{v(\mathbf{e})} = \frac{(\mathbf{e}\mathbf{n})}{\varrho(\mathbf{e})} \left\{ m^*(\mathbf{e}) - \frac{1}{2\pi} \int_0^{2\pi} d\varphi \int_0^1 \frac{\partial m^*(\cos \theta, \varphi)}{\partial (\cos \theta)} \frac{d \cos \theta}{\cos \theta} \right\}. \quad (9.7)$$



Knowing the shape of the surface  $\rho(\mathbf{e})$ , we can find the volume contained within it and thus determine the number of electrons in the corresponding zone.

The observation of the de Haas–van Alphen effect in thin single crystal films opens up new possibilities for determining the shape of the Fermi surface.<sup>[33]</sup> According to Sec. 8, for this purpose we can use the fact that the contribution of those electrons whose orbit size exceeds the transverse dimensions of the film is much less than that of electrons whose orbits are contained within the film. Since the orbit size is inversely proportional to the magnetic field strength, a change in the magnetic field will lead to a marked increase (for  $H = H_C$ ) of the quantum oscillations with a definite period, which is determined by those electrons whose orbits “got into” the film. If the magnetic field is parallel to the film surface, the critical field  $H_C$  (the field at which one observes an abrupt change in the oscillation amplitude) determines the diameter  $D$  of the section of the Fermi surface in the direction perpendicular to the magnetic field and normal to the surface of the film:

$$D = \left| \frac{eH_C d}{c} \right|,$$

where  $d$  is the film thickness. By changing the field direction and using different orientations of the film, one can in principle construct the Fermi surface directly from the diameters  $D$ . The advantage of this method of determining the shape of the Fermi surface is that the film itself produces something resembling a Fourier analysis. Since the curves of the dependence of magnetic moment on magnetic field are extremely complicated (as a rule the oscillations contain a large number of harmonics), unscrambling the experimental is a problem which is very difficult and sometimes cannot be solved unambiguously. The use of thin films might help solve the problem. But the final deciphering of the electronic structure is possible only by using the results of many different kinds of experiments.

In concluding this section we note that observation of the de Haas–van Alphen effect has made it possible to unravel the structure of many metals.

## 10. GENERAL THEORY OF OSCILLATORY PHENOMENA<sup>[44]</sup>

The treatment of oscillations of thermodynamic quantities in a magnetic field (Secs. 6–9) shows that their origin is the oscillation of the density of states, and that the effect of the magnetic field is simply to quantize the energy levels. Obviously similar effects should occur whenever conditions are present which cause a quantization of the energy. One should then observe an oscillatory dependence on the parameters which determine the position of the energy levels of the electron, provided the distance between levels is

the order of or larger than the temperature, but much less than the Fermi energy.

One can develop a general theory of oscillation phenomena by using the equations for quasiclassical quantization, according to which the adiabatic invariants  $I_i$  of a system which carries out a finite motion are equated to half-integral multiples of Planck's constant:

$$I_i = \left( n_i + \frac{1}{2} \right) h, \quad n_i = 0, 1, 2, \dots \quad (10.1)$$

If the “classical” problem of the motion of an electron with an arbitrary dispersion law has been solved, its energy can be expressed in terms of the adiabatic invariants

$$\varepsilon = \varepsilon(I_1, I_2, I_3),$$

so that, by using (10.1), one can get a quantization of the energy levels:

$$\varepsilon(\mathbf{n}) = \varepsilon \left[ \left( n_1 + \frac{1}{2} \right) h, \left( n_2 + \frac{1}{2} \right) h, \left( n_3 + \frac{1}{2} \right) h \right]. \quad (10.2)$$

The vector  $\mathbf{n}$  stands for the three integers  $n_1$ ,  $n_2$ , and  $n_3$ .

The use of quasiclassical energy levels makes the whole theory applicable only to the case where the distance between levels is much less than the limiting energy  $\varepsilon_F$ . This approximation is sufficient since (as we have said repeatedly) oscillations appear only in this limiting case.

The quantization condition (6.7), which was applied earlier is, of course, a special case of (10.2). In the case of an electron moving in a magnetic field, the adiabatic invariant is the quantity  $cS/eH$ .

Knowing the quantum energy levels (10.2) enables one to compute the oscillatory part of the thermodynamic potential

$$\Omega = -T \sum_{\mathbf{n}} \ln \left\{ 1 + e^{\frac{\varepsilon - \varepsilon(\mathbf{n})}{T}} \right\}.$$

Using the three-dimensional analog of the Poisson formula, we have

$$\Omega = -T \int \ln \left\{ 1 + e^{\frac{\varepsilon - \varepsilon(\mathbf{n})}{T}} \right\} d\mathbf{n} + 2 \operatorname{Re} \sum_{\mathbf{k}} L_{\mathbf{k}} + \dots \quad (10.3)$$

where

$$L_{\mathbf{k}} = -T \int \ln \left\{ 1 + e^{\frac{\varepsilon - \varepsilon(\mathbf{n})}{T}} \right\} e^{2\pi i \mathbf{k} \cdot \mathbf{n}} d\mathbf{n},$$

while the vector  $\mathbf{k}$  stands for the set of three integral subscripts  $k_1$ ,  $k_2$ , and  $k_3$ . The summation is over all positive values of  $k_i$  ( $i = 1, 2, 3$ ) except  $k_i = 0$ .

Since the integration over  $\mathbf{n}$  is only over the first octant ( $0 \leq n_i \leq \infty$ ,  $i = 1, 2, 3$ ), because of the discontinuity of the integrand at the boundary of the region of integration, in addition to the three-dimensional integrals there are also two-dimensional and one-dimensional integrals, whose explicit form we shall not give.

Carrying out computations similar to those in Sec. 6, we find that the oscillating part of  $L_{\mathbf{k}}$  has the following form:

$$\tilde{L}_{\mathbf{k}} = \frac{1}{(2\pi)^2} \frac{1}{\sqrt{k_1^2 + k_2^2 + k_3^2}} \sum_{\nu} \frac{\psi(\lambda_{\mathbf{k}}) e^{2\pi i \mathbf{k} \cdot \mathbf{n}_{\nu}(\mathbf{k}, \zeta) + i \varphi_{\nu}}}{\left( \mathbf{k} \frac{\partial \mathbf{n}_{\nu}}{\partial \zeta} \right)^2 |\nabla \epsilon(\mathbf{n}_{\nu})| |K_{\nu}(\zeta)|} \quad (10.4)$$

Here  $\mathbf{n}_{\nu} = \mathbf{n}_{\nu}(\mathbf{k}, \zeta)$  denotes the radius vector in the  $\mathbf{n}$  space to those points of the surface  $\epsilon(\mathbf{n}) = \zeta$  at which the direction of the normal to the surface is parallel to the vector  $\mathbf{k}$ ;  $K_{\nu}(\zeta)$  is the Gauss curvature of the surface at these points,  $\lambda_{\mathbf{k}} = 2\pi^2(\mathbf{k} \cdot \partial \mathbf{n}_{\nu} / \partial \zeta)T$ ,  $\varphi_{\nu} = \pm \pi/2$  if  $\mathbf{n}_{\nu}$  is an elliptical point; the minus sign applies to the case where the convexity of the surface at the given point is toward  $\mathbf{k}$  while the plus sign is used in the opposite case. In the case of a hyperbolic point,  $\varphi_{\nu} = 0$ . Again we shall not write the two-dimensional and one-dimensional terms.

Substituting the asymptotic expressions for  $L_{\mathbf{k}}$  (10.4) and the two-dimensional and one-dimensional terms which we have omitted in formula (10.3), we get the oscillatory part of the potential  $\Omega$ . To compute the period of oscillation we must know the dependence of the  $\mathbf{n}_{\nu}$ , i.e., of the adiabatic invariants  $I_i$ , on the parameters which determine the position of the quantized energy levels; from formula (10.4) we see that the periods of oscillation are given by the condition

$$\Delta I_i^{(\nu)} = h,$$

where the symbol  $\Delta I_i$  denotes the change in the  $i$ -th adiabatic invariant because of a change in the parameters determining the finite motion of the electron. It should be remembered that  $\tilde{\Omega}$  is the sum of a large number of terms, all of the same order, each of which has its own period. Since in general the ratios of these periods are arbitrary, the oscillations can take on very complicated forms.

## APPENDIX

### 1. THE DEFINITION OF THE EFFECTIVE MASS OF A CONDUCTION ELECTRON

The dynamical properties of a free electron are determined completely by its mass. As was shown in [1], the dynamics of a conduction electron depend essentially on its dispersion law. In this connection the introduction of an "effective mass" is not a unique procedure. In [1] the effective mass  $m^*$  was introduced using the expression for the period of the motion in a magnetic field. Such a definition is convenient since  $m^*$  retains its value when the electron moves in the magnetic field. For motion in weak fields (electric and magnetic), where, in the linear approximation in the force acting on the electron, one can neglect the change in the quasimomentum of the electron during a free path (if we are interested in its spatial motion),

it is convenient to use the concept of an "inverse effective mass tensor."

The classical equation of motion of the electron has the form [1]

$$\frac{d p_i}{d t} = F_i, \quad v_i = \frac{\partial \epsilon}{\partial p_i}.$$

Since  $v_i = dx_i/dt$ , we then get

$$\frac{d^2 x_i}{d t^2} = \frac{\partial^2 \epsilon}{\partial p_i \partial p_k} F_k. \quad (A.1)$$

If we omit nonlinear terms in the force, the tensor  $\partial^2 \epsilon / \partial p_i \partial p_k$  can be assumed to be a constant. It is called the inverse effective mass tensor, and is denoted by  $(1/m)_{ik}$ :

$$\left( \frac{1}{m} \right)_{ik} = \frac{\partial^2 \epsilon}{\partial p_i \partial p_k}. \quad (A.2)$$

We should mention that at an arbitrary point of  $\mathbf{p}$ -space, the three principal values of the inverse effective mass tensor do not all have the same magnitude or the same sign ( $1/m_1 \neq 1/m_2 \neq 1/m_3$ ). Near energy minima and maxima, the principal values  $1/m_i$  of the effective mass tensor have the same sign ( $1/m_i < 0$  near a minimum,  $1/m_i > 0$  near a maximum).

### 2. MOTION IN A TIME-VARYING, INHOMOGENEOUS ELECTROMAGNETIC FIELD

In a constant magnetic field of intensity  $H$ , an electron which is on a closed constant-energy surface moves along a trajectory which is given by the equations (cf. Sec. 3 in [1])

$$p_H = \text{const}, \quad \epsilon(p_x, p_y, p_H) = \text{const}. \quad (A.3)$$

In this case the moving electron is similar to a current loop.

As the treatment in [45] shows, the motion in a slowly varying, weakly inhomogeneous magnetic field can be pictured as a drift, rotation and deformation of the "current loop," where the nature of this slow motion is easily established from the fact that the ratio of the area of the section of the constant-energy surface  $S$  to the magnetic field  $H$  is an adiabatic invariant.\* We also note that in this case the velocity of the center of the current loop coincides at each point with the direction of the magnetic field.

If Eq. (A.3) describes an open trajectory, we must distinguish two cases:

a) Curve (A.3) is periodic, i.e., the direction in which it is open is parallel to some vector of the reciprocal lattice. The principal difference from the

\*If the magnetic field is a slowly varying function of the time, the statement that  $S/H$  is an adiabatic invariant is clear from the quantization condition [cf. formula (6.8)]. If  $\mathbf{H}(\mathbf{r})$  is a slowly varying function of the coordinates, the equations of motion of the electron have an extremely simple form:

$$\frac{S(\epsilon, p_H)}{H(\mathbf{r})} = \text{const}, \quad \epsilon = \text{const}, \quad \dot{\mathbf{r}} = \frac{\partial \epsilon}{\partial \mathbf{p}}.$$

case of closed sections is that the velocity is not directed along the magnetic force line, as a result of which  $S/H$  is not an adiabatic invariant. However, the general nature of the motion is very similar to the motion in a closed trajectory. Thus the role of the period is taken by the time during which the electron passes through a unit cell of the reciprocal lattice.

b) Curve (A.3) is not periodic, i.e., the direction in which it is open is not parallel to any vector of the reciprocal lattice.

In averaging over an aperiodic trajectory, the integration along the open trajectory passing through an infinite set of unit cells\* can be replaced by a sum of integrals over equivalent segments within one cell (Fig. 20). In the case of an aperiodic trajectory, these segments are everywhere dense in the unit cell.

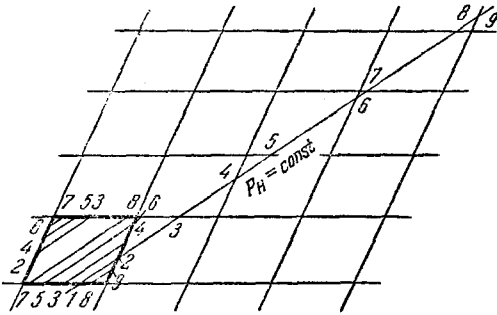


FIG. 20. One of the crystal planes of the reciprocal lattice, cut by the plane  $p_H = \text{const}$ . The same number is used to mark equivalent points.

It then follows that the averaged quantities describing the slow motion cannot depend on  $p_H$ , the projection of the momentum along the magnetic field. Naturally the dependence of the averages on  $p_H$  can also be neglected for periodic trajectories if their period is much greater than  $\hbar/a$  ( $a$  is the average spacing between atoms). This fact (that the averages are independent of  $p_H$ ) causes a fundamental change in the character of the slow motion.

The most interesting situation occurs when, during the motion in a field which is slowly varying in space and time, a transition occurs from one type of motion to another. When this occurs we get a phenomenon which is very similar to the scattering by a center of force.

The regions in  $p$ -space with different types of motion are separated from one another by the segments

\*Actually, the derivation of the equations describing the slow motion (drift, etc.) involves averaging over a time interval  $T$  which satisfies the inequality  $T_0 \ll T \ll \tau$ , where  $T_0$  is the time for the electron to traverse a unit cell and  $\tau$  is the mean free time. But in averaging bounded quantities, the integration can be extended over the entire trajectory, since the difference

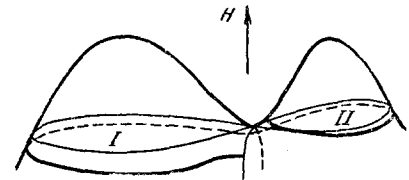
$$\lim_{T' \rightarrow \infty} \frac{1}{2T'} \int_{-T'}^{T'} f(t') dt' - \frac{1}{T} \int_t^{t+T} f(t') dt'$$

is a rapidly oscillating function of order  $fT_0/T$ .

of the self-intersecting trajectories which are formed on the section of the surface  $\epsilon = \text{const}$  by the plane tangent at the hyperbolic points of the constant-energy surface. These points are the classical stagnation surfaces for motion in a homogeneous constant magnetic field. The period of motion of the particle diverges logarithmically as  $p_H \rightarrow p_H^k$  (where  $p_H^k$  is the vector in  $p$ -space drawn at the singular point).

The essence of the scattering phenomenon is most easily explained on the example of motion in a weakly inhomogeneous magnetic field which is constant in time and has straight lines of force. Let  $F$  be a saddle point of the constant-energy surface  $\epsilon = \epsilon_0$  such that the normal to the surface at this point is parallel to  $H_0$ . The section  $\epsilon = \epsilon_0$ ,  $p_H = p_H^k$  is a figure-8, whose crossing point is at  $F$ . If the current loop during its motion in  $p$ -space, touches the surface at the saddle point, it will later split into two current loops, corresponding to the regions I and II, separated by the singular point (Fig. 21). The types of motion in these two regions are essentially different. Depending on the exact "microscopic" initial conditions, the particle falls either into region I or into region II.

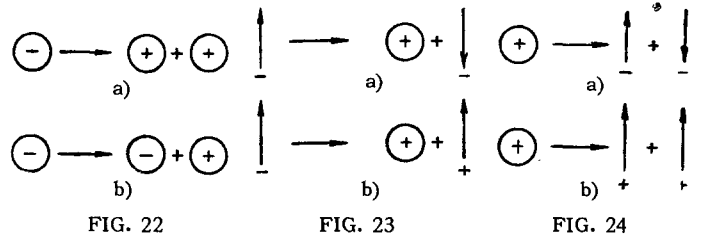
FIG. 21. Motion of an electron in an inhomogeneous magnetic field near a saddle point of the constant-energy surface (splitting off of a current loop).



The "microscopic" initial conditions alternate so that in each microscopic element of the energy surface, determined by the averaged values of the "coordinates," there are points from which the particle goes into region I and points from which it goes into region II. From this point of view one can regard the falling of the particle into the two regions as a random process and speak of a "scattering" of the particles near the singular point; the probabilities for scattering into I and II ( $w_1$  and  $w_2$ ) have well-defined values.

To determine the scattering probabilities  $w_1$  and  $w_2$ , we consider a classical ensemble of particles distributed according to some impact parameter, whose choice will be made later. Each particle, during its last turn before falling into region I and II, intersects the principal line of curvature, passing through the point  $F$  (point  $p_2 = 0$  in Fig. 20) for some value of  $p_H(0)$ . After making one complete turn around one of the loops of the figure-8, the particle is again in the neighborhood of the crossing point. Depending on the sign of the difference  $p_H(t) - p_H$  at that time, the particle enters region I or region II; the quantity  $p_H(t) - p_H$  is uniquely determined by the value of  $p_H(0)$  at the start of the revolution. From this we see that  $p_H(0)$  serves as a convenient impact parameter. To the regions I and II there correspond ele-

Types of transition from one type of motion to another.  $\circ$  — motion in a closed trajectory;  $\uparrow$  — motion in an open trajectory (the symbols are explained in the text).



Types of constant-energy surfaces corresponding to the transitions shown in Figs. 22-24.



ments  $\delta_1$  and  $\delta_2$  of the values of  $p_H(0)$ , determining whether the particle enters the particular region. The scattering probabilities  $w_1$  and  $w_2$ , i.e., the relative numbers of particles entering I and II, respectively, are proportional to the flux of particles through  $\delta_1$  and  $\delta_2$ . For a sufficiently smooth distribution function, in first approximation in the inhomogeneity, these fluxes are given for a sufficiently smooth distribution function by the sizes of the elements themselves.

The intervals  $\delta_1$  and  $\delta_2$  are determined using the relation

$$p_H(t) = p_H(0) + \int_0^t \dot{p}_H dt'$$

We then find that

$$\delta_1 = \int_0^{T_1} \dot{p}_H dt', \quad \delta_2 = \int_{T_1}^{T_2} \dot{p}_H dt'. \tag{A.4}$$

(Here  $T_1$  is the time for traversing the first loop of the figure-8, and  $T_2$  is the time for going around the whole figure-8.

The main contribution to the change in  $p_H$  during the time of traversal of the figure-8 comes from the part of the trajectory which is far from the singular point. The reason for this is that  $\dot{p}_H = 0$  at the singular point.

Using the equation of motion of a current loop, one can show that (A.4) leads to [45]

$$\frac{w_1}{w_2} = \frac{\delta_1}{\delta_2} = \frac{S_1}{S_2}, \tag{A.5}$$

where  $S_1$  and  $S_2$  are the areas of the loops of the figure-8. From (A.5) we have

$$w_1 = \frac{S_1}{S_1 + S_2}, \quad w_2 = \frac{S_2}{S_1 + S_2}$$

In the general case there are several types of transition from one regime to the other. The possible types of transitions are shown schematically in Figs. 22-24. On the right of each diagram are the symbols corresponding to the two regions where the scattering occurs. The circles represent the closed trajectory; the arrow corresponds to an open periodic trajectory,

the direction of the arrow giving the direction of motion along the periodic trajectory. The types of constant-energy surfaces corresponding to these transitions are shown in Figs. 25-27, where the lines  $p_H = \text{const}$  are drawn. The point of self-intersection is labelled F. The thick line is the self-intersecting curve. The arrows show the direction of motion along the trajectory. Figure 25 corresponds to diagrams 22a and b; Figure 26 to diagrams 23a and 24a; Figure 27 to diagrams 23b and 24b. The signs in Figs. 22-24 are the same as the sign of the difference  $p_H - f_H$  in the regions with different types of motion.\*

For motion in an arbitrarily weak inhomogeneous electromagnetic field which varies slowly with time, the derivation of the probabilities of different types of motion is somewhat more complicated than the special case treated above. In [45] compact expressions for the probabilities in the most interesting special cases were obtained from the general formula. For example, for motion in a weak electric field parallel to a constant, homogeneous magnetic field:

$$\frac{w_1}{w_2} = \left. \frac{\frac{d}{dp_H} S_1(p_H, e_{\text{ep}}(p_H))}{\frac{d}{dp_H} S_2(p_H, e_{\text{ep}}(p_H))} \right|_{p_H = p_H^k}$$

### 3. QUASICLASSICAL QUANTIZATION NEAR SINGULAR CLASSICAL TRAJECTORIES

As was shown in the first part of this survey (cf. Sec. 3), the period of motion of the electron along the self-intersecting trajectory is logarithmically infinite, since the point where the curve intersects itself is a stagnation point.

If one disregards overlapping of zones (cf. Sec. 1), the figure-8 trajectories are the most general type of singular trajectory. In Fig. 28 we show typical tra-

\*Six other types of transition, which do not differ basically from those shown in Figs. 22-24, are obtained by reversing the sign.

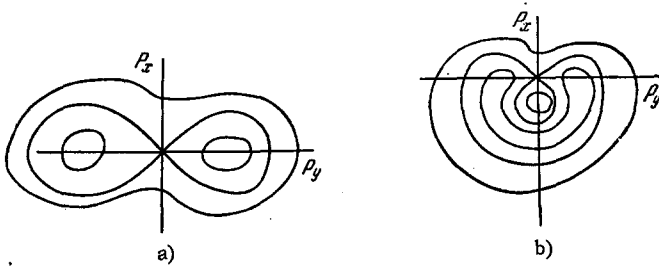


FIG. 28. Typical singular trajectories in a magnetic field near a point of self-intersection. a) constant-energy surface has a bridge; b) constant-energy surface has a dimple.

jectories in a magnetic field. To the different trajectories there correspond different values of  $p_z$ . Figure 28a shows a section of the constant-energy surface near a bridge, and Fig. 28b near a dimple. The singular trajectory corresponds to  $p_z = p_{zk}$ .

To sufficient accuracy (i.e., to the accuracy necessary for computing the oscillating parts of the thermodynamic potential, cf. Sec. 6), the quasiclassical energy levels can be gotten from the usual condition for "quantization of area" (Sec. 5 of [1]). However, in finding the energy levels one must take into account that at  $p_z = p_{zk}$  the area  $S$  has a singularity of the type  $\Delta p_z \ln \Delta p_z$ , where  $\Delta p_z = p - p_{zk}$ . On one side of  $p_z = p_{zk}$  there are two systems of quasiequidistant levels\* given by the equations

$$S_1(\epsilon, p_z) = \frac{ehH}{c} n_1, \quad S_2(\epsilon, p_z) = \frac{ehH}{c} n_2. \quad (\text{A.6})$$

On the other side there is one system, given by the equation

$$S(\epsilon, p_z) = \frac{ehH}{c} n. \quad (\text{A.7})$$

"Readjustment" of the levels occurs near  $p_z = p_{zk}$  and is described by the system of equations

$$\begin{aligned} S_{1k} + p_0 \Delta p_z \ln \left| \frac{\Delta p_z}{p_0} \right| &= \frac{ehH}{c} n_1, \\ S_{2k} + p_0 \Delta p_z \ln \left| \frac{\Delta p_z}{p_0} \right| &= \frac{ehH}{c} n_2, \\ S_k + p_0 \Delta p_z \ln \left| \frac{\Delta p_z}{p_0} \right| &= \frac{ehH}{c} n, \quad S_k = S_{1k} + S_{2k}, \end{aligned} \quad (\text{A.8})$$

where  $p_0 = 2V_z(p_{zk}) \sqrt{m_1 m_2}$ . Introducing the notation

$$\frac{cS_{1k}}{ehH} = n_{1k}, \quad \frac{cS_{2k}}{ehH} = n_{2k}, \quad \frac{cS_k}{ehH} = n_k,$$

we have from Eqs. (A.8),

$$\begin{aligned} \Delta p_z &= \frac{eHh}{cp_0} \frac{n_1 - n_{1k}}{\ln \frac{ehH}{cp_0} (n_1 - n_{1k})}, \\ \Delta p_z &= \frac{eHh}{cp_0} \frac{n_2 - n_{2k}}{\ln \frac{ehH}{cp_0} (n_2 - n_{2k})}, \quad \Delta p_z = \frac{eHh}{cp_0} \frac{n - n_k}{\ln \frac{ehH}{cp_0} (n - n_k)}. \end{aligned} \quad (\text{A.9})$$

\*To be specific, we have assumed that the energy is fixed, so that  $p_z$  is quantized ( $p_{zk}$  is a function of the energy). Naturally, if  $p_z$  is fixed the energy  $\epsilon$  is quantized. The singular trajectory corresponds to a definite critical value of the energy  $\epsilon_k = \epsilon_k(p_z)$ .

It is interesting to note that near  $p_z = p_{zk}$  the distances between levels are not at all equivalent; we have seen that this result is a consequence of the quasiclassical quantization conditions. Equations (A.8) are applicable for  $n_{1k}$ ,  $n_{2k}$ , and  $n_k \gg 1$ , while the solutions (A.9) hold only for  $n_{1k}$ ,  $n_{2k}$ ,  $n_k \gg |n - n_{1k}|$ ,  $|n - n_{2k}|$ ,  $|n - n_k| \gg 1$ . A rigorous quantum mechanical treatment in the quasiclassical approximation for the motion of electrons along figure-8 trajectories, given by Zil'berman [46] and much more completely by Azbel', [47] leads to similar results.

We also mention that more accurate quasiclassical trajectories (including the  $\frac{1}{2}$  in the Bohr quantization conditions) show that there is a peculiar oscillatory dependence of the level separation on magnetic field (Azbel', [47]).

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Translated by M. Hamermesh