# MAGNETISM AND ELECTRICAL CONDUCTIVITY OF METALS

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This paper gives a summary of the present state of the theory of magnetic and electrical properties of matter in the metallic state. In this survey we cannot avoid recalling the great contribution which was made to the development of the present quantum theory of solids in general and to the theory of metals in particular by Jacob Il'ich Frenkel, one of the great theoretical physicists of the first half of our century.

At the start of the scientific activity of J. I. Frenkel (in the Twenties), there arose in the electron theory of metals, which had its beginnings in the work of Drude and Lorentz (cf., for example,[1]), a difficult situation, since the classical statistical foundations of this theory were completely compromised by the well-known catastrophe in the theory of the specific heat of an electron gas. At the same time there had already occurred the development of the Bohr quantum theory of the atom and the beginning of the building up of a consistent quantum mechanics. It was in just this period that there appeared the papers of J. I. Frenkel in which, with his profound physical intuition and theoretical talent, he placed the first building blocks in that strong foundation on which there later developed the great structure of the present-day quantum theory of solids. In connection with the theme of this paper we recall from the many articles of J. I. Frenkel four papers which are of fundamental significance; they contain essentially many of the elements of the present theoretical treatment of magnetic and electrical properties of metals.

The first of these papers[2] was published in 1924 and is entitled "Theory of the Electrical Conductivity of Metals." In it, for the first time, on the basis of the Bohr picture of the nuclear structure of the atom, there was given a quantitative formulation of the idea of electrons wandering around in a metal, which appear as the result of collectivization of the valence electrons of the isolated atoms of metallic elements when they are condensed in the form of a metal. Frenkel's calculation retained completely all of the positive results of the classical Drude-Lorentz electron theory of metals (including the important derivation of the Wiedemann-Franz law) and at the same time completely eliminated the difficulty with the specific heat, since the electrons of a Bohr atom even at 0°K have a large zero-point energy. It was this paper of J. I. Frenkel which should also be regarded as the beginning of the present theory of collectivized conduction electrons in crystals of metallic type. This theory of migrating electrons, which solved the difficulty with the specific heat and rehabilitated the very hypothesis of conduction electrons in metals, could not,

however, at that time explain the differences between metals and dielectrics. (For dielectrics one was required to introduce additional assumptions about the absence of collectivized electrons.) In addition, there remained open the question of why the mean free path of conduction electrons is so large at low temperatures if it is determined from the magnitude of the specific electric and thermal conductivity of metals. The approach to the solution of these difficulties in the theory of migrating electrons was indicated in another paper of J. I. Frenkel[3] written by him in 1927 and presented at the International Physics Conference in Como (Italy); this paper was entitled, "A New Development in the Electron Theory of Metals." In this paper for the first time modern quantum mechanics was applied to the solution of problems of metals; it was shown that specific properties of electrons in a crystal lattice, and in particular the anomalously large value of the mean free path of conduction electrons (compared to the size of the lattice constant a) can be explained by starting from the concept of the wave nature of the electron. An ideal regular lattice, according to the laws of quantum mechanics, is "transparent" to the electron waves. Only a disturbance in the regularity of the crystals (interstitial atoms and displacements, vacancies at lattice sites, dislocations, disordered thermal vibrations of lattice atoms, etc.) lead to a scattering of the electron waves. It is this picture, presented in the report of J. I. Frenkel at Como, which lies at the basis of the whole present-day theory of kinetic effects in crystals.

The third paper of J. I. Frenkel which should be mentioned here was published by him in 1928[4] and was called "Elementary Theory of Magnetic and Electric Properties of Metals at Absolute Zero." The most significant part of this exceptionally simple and clear, but at the same time physically profound work is Sec. 2, in which he gives the first quantum mechanical explanation of the phenomenon of ferromagnetism in metals, as a purely electrical effect resulting from exchange electrostatic interactions between electrons in metals of the transition groups. This derivation may with complete justification be regarded as the beginning of the whole present-day quantum theory of ferromagnetism (theory of spontaneous magnetization).* From the point of view of models, this paper can be regarded as the starting point in the

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*The paper of W. Heisenberg,[5] in which a similar explanation of the quantum mechanical nature of ferromagnetism was given on the basis of a model of localized electrons, was published after the paper of J. I. Frenkel.[4]

construction of the theory of ferromagnetism on the basis of the so-called collective electron model.

Finally, the fourth paper of J. I. Frenkel[7] was written by him in collaboration with Ya. G. Dorfman in 1930 and is entitled, "Spontaneous and Induced Magnetization in Ferromagnetic Materials." The authors of this paper deserve the credit for the first theoretical clarification of the hypothesis of regions of spontaneous magnetization, which is at the basis of the whole present physical theory of magnetization processes in ferromagnets (cf., for example, [8]).

Of course, these four papers which we have mentioned do not exhaust the whole rich contribution to the science of solids and metals which was made by J. I. Frenkel in his scientific work, but these papers are already enough so that one may with full justification regard J. I. Frenkel as one of the founders of the present quantum theory of metals.*

## 1. FUNDAMENTAL ELECTRONIC CHARACTERISTICS OF THE METALLIC STATE OF MATTER

Before we characterize the present situation in the theory of magnetic properties and electrical conductivity of crystals, we must recall the basic physical feature of the metallic state, whose existence enables us to speak of metals as substances of a separate class which can be uniquely distinguished from all other materials. This fundamental characteristic is the presence in metallic crystals of the system of conduction electrons of which we have already spoken.† What properties do these conduction electrons have? First we must point out that these microparticles are Fermi particles having special quantum characteristics.[14] The many-electron wave function of a system of Fermi particles describing the quantum states is antisymmetric‡ with respect to interchange of the coordinates of any pair of particles in the system. This one fact already produces a very essential statistical correlation in the motion of Fermi particles (the Pauli principle[14]). The energy spectrum of such a system also has various characteristic features. These can most easily be explained if we first recall the properties of an ideal gas of Fermi particles, i.e., a gas of dynamically non-interacting conduction electrons. Because of the antisymmetry of the wave function of the gas (which for an ideal gas

*To become familiar with the original papers of J. I. Frenkel on the problems of the physics of metals, we recommend to the readers his monograph on the subject[9] and also the second volume of the Collected Works (Sec. I);[10] cf. also his paper at the Kurnakovskiĭ lectures.[11]

†More details concerning the empirical criteria for the metallic state of matter can be found, for example, in the survey by the author[12] or by the author and V. I. Arkharov.[13]

‡That is, the wave function of the system changes sign when we interchange the coordinates of any pair (i, k = 1, 2, 3, ... , N) of particles:

$$\Psi\,(r_1,\ r_2,\ \ldots,\ r_i,\ \ldots,\ r_k,\ \ldots,\ r_N)$$
$$= -\Psi\,(r_1,\ r_2,\ \ldots,\ r_k,\ \ldots,\ r_i,\ \ldots,\ r_N).$$
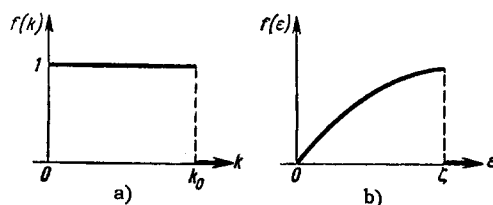


FIG. 1. Distribution function for an ideal gas of fermions: a) as a function of quasimomentum ℏk (or wave number k); b) as a function of energy ε for the case of a quadratic dispersion law. The quantities $k_0$ and $\zeta$ are respectively the limiting wave number and the limiting Fermi energy.

has the form of a determinant made up from the wave functions of the individual electrons), the Pauli principle holds in it, according to which in each quantum state with a given quasimomentum k there can be at most one electron with a given spin projection $\sigma^2$ ($\sigma^2 = \pm\,\hbar/2$). As is well known, it then follows[14] that the distribution function (whose values give the relative number of occupied states with a given k) f(k) in the ground state, with the lowest value of the energy of the system (at 0°K), has the form of "a Fermi step"[14] (Fig. 1a). Thus, in the quasimomentum space ℏk there is a certain surface, the <u>Fermi surface</u>, which corresponds to the quantum state with the maximum electron energy ε(k) = $\epsilon_0$ occupied by them at 0°K. The "internal" region of k-space which is limited by the Fermi surface (the energy values being less than this value: ε < $\epsilon_0$) corresponds to occupied states, i.e., to those with f(k) = 1, while the "outside" region, outside the Fermi surface (with larger energy: ε > $\epsilon_0$), corresponds to free states, i.e., to those with f(k) = 0. If the gas of conduction electrons is ideal, then the dispersion law has the usual quadratic character*

$$\varepsilon\,(k) = \frac{\hbar^2}{2m}\,k^2, \tag{1.1}$$

where 2πℏ is Planck's constant and m is the mass of a free electron. The Fermi surface in this case has the form of a sphere whose radius (ℏ$k_0$) is determined by the density of the electron gas n, since n = $(8\pi/3)k_0^3$.[14] In a real crystal the conduction electrons do not form an ideal gas of free particles moving in a zero potential field. In this case each conduction electron moves in the periodic, self-consistent field produced first of all by the atomic nuclei and the non-collectivized inner electron shells of the atoms which form in the aggregate a crystal lattice of "heavy" positively-charged <u>ion cores</u>, and secondly by all the other collectivized electrons. The quantum mechanical solution of the problem in such a self-consistent, periodic field (Bloch,[15] Peierls[16]) showed that the energy spectrum ε(k) of an individual electron has a <u>band structure</u>, i.e., it exhibits a series of quasi-continuous energy bands separated by regions of forbidden energies

*The energy distribution function f(ε) in this case will have the form of a "parabola," cutting off at $\epsilon_0$ = $\zeta$ (cf. Fig. 1b).
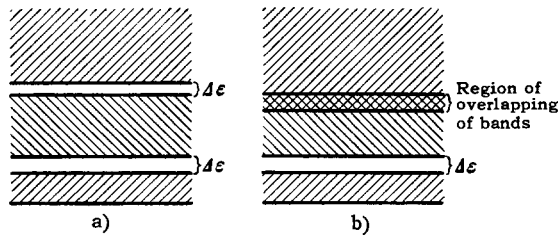
FIG. 2. Energy spectrum of collectivized electrons in a crystal lattice showing quasi-continuous bands of allowed energy values (shaded regions): a) separated by forbidden regions (energy gaps $\Delta\varepsilon$) or, b) partially overlapping.



FIG. 3. Filling of energy levels of bands of allowed energy values of the electron energy spectrum in crystals in the ground state (at $0°K$). a) Metal with non-overlapping bands; b) semiconductor or insulator; c) metal with overlapping bands.

(gaps) or shows a partial overlap (Fig. 2). The wave function of the electron then has the form of a plane wave modulated with the period of the lattice:

$$\Psi_n(\mathbf{k}, \ \mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_n(\mathbf{k}, \ \mathbf{r}), \tag{1.2}$$

where $\hbar\mathbf{k}$ is the quasi-momentum vector which plays the role of a quantum number, n numbers the band (zone), and $u_n(\mathbf{k}, \mathbf{r})$ is a function with the period of the crystal lattice. From the form of the function (1.2) it follows that the electron can be found with equal probability at any site in the lattice. This also defines the "freedom" of the conduction electron in the periodic field of the lattice. The form of the modulating function $u_n(\mathbf{k}, \mathbf{r})$, aside from its symmetry properties which are determined by the crystal symmetry, depends on the specific form and magnitude of the potential energy of the electron in the lattice. It is also essential to note that the dispersion law $\varepsilon(\mathbf{k})$ for an electron in a lattice no longer has the simple quadratic character (1.1), but can have a very complex form which is determined both by the symmetry properties of the crystal (since the function $\varepsilon(\mathbf{k})$ is a periodic function of $\mathbf{k}$ with a period proportional to the period of the reciprocal lattice,[14] and is also a multiple-valued function of $\mathbf{k}$ —for different bands and a specific form of the lattice potential). The complex nature of the dispersion law $\varepsilon(\mathbf{k})$ for an electron in a crystal is a mathematical and physical expression of the fact that the electron under these conditions is not a "free" microparticle, and that essentially we are dealing with a more complicated quantum-mechanical system: electron + lattice of ion cores (the latter, in view of its large mass, can be treated as a fixed source of a force field*); therefore the conduction electron in a metal, within the framework of the band model, should be treated as a sort of quasiparticle (cf. below), having a more complicated dispersion law than the free electron. In certain special cases (and for a restricted range of values of the quasi-momenta, for example,

near the extrema of the energy surfaces $\varepsilon(\mathbf{k}) = \mathrm{const}$), the energy of an electron in a lattice can be given formally in a form analogous to (1.1), but with the mass of the free electron m replaced by another quantity $m_{eff}$, which is called the effective mass of the electron in the lattice:

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2}{2m_{eff}} k^2 \tag{1.3}$$

and we treat the whole aggregate of electrons as a gas of quasiparticles with effective masses.* Since in the case of a complex dispersion law the conduction electrons in the band theory are still Fermi particles, for them also we have the same distribution function in the ground state (cf. Fig. 1) and there exists a Fermi surface: $\varepsilon(\mathbf{k}) = \epsilon_0 = \zeta$. Only now this surface in the general (non-isotropic) case does not have the form of a sphere, but is some complicated surface determined by the form of the function $\varepsilon(\mathbf{k})$. Since the energy spectrum of an electron in the crystal has the form of bands separated by forbidden regions, in filling up the energy levels with electrons for the ground state we may expect two cases to occur: Either the Fermi energy $\zeta$ corresponds to a level within an allowed band, or it just coincides with the uppermost level of one of the bands, just at the edge of a gap (Fig. 3).[†] In the first case the energies of the excited states of the system will not be separated from the energy of the ground state by a gap (the case of a metal), while in the second case there will be a gap (the case of an insulator or semiconductor). Thus the band theory gives a criterion for the metallic and non-metallic states of matter.[12] The great success of the band theory included also the achievement of the following important results: the determination of the linear dependence on

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*In other words we are dealing with the so-called adiabatic approximation. Including the motion of the ionic lattice is necessary in calculating the kinetic coefficients, which depend essentially on lattice vibrations, for phenomena of superconductivity, or effects of polarization of the lattice, as, for example, in ionic crystals, etc.
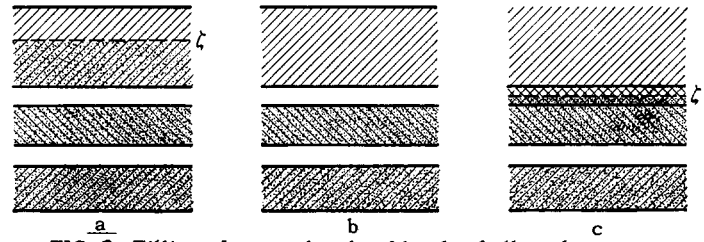
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*The effective mass method[17] is a special case of mass renormalization, which is widely used in quantum electrodynamics.[18]

†One should not think that having the energy $\epsilon_0 = \zeta$ coincide with the upper edge of the allowed band is a rare exceptional case. The point is that the number of levels (places) in the band is equal to twice the number of lattice sites (because of the spin degeneracy), so that for divalent atoms the number of electrons is precisely equal to the number of levels in the band. However, such a situation will not occur for all crystals made up of divalent atoms, since the bands may overlap and then $\epsilon_0 = \zeta$ will always lie "within" a band (cf. Fig. 3b).

temperature for the electronic specific heat of metals, [19] the temperature behavior of electric and thermal conductivity, [14] the weak paramagnetism of metals (Pauli[20]), the diamagnetism of conduction electrons (Landau[21]), and others. It is important to point out that all the results of band theory which agree with experiment arise not from the specific form of the dispersion law $\epsilon(k)$, which usually was selected from crude models, but rather from the general statistical properties of the conduction electrons, from the fact that they form a system of fermions.*

In connection with our last remark, one can a priori imagine the following two alternative possibilities for the further development of the theory of metals. First, it might be that on the basis of the successes of the band theory in its one-electron variant, one might simply postulate that the conduction electrons form a system of non-interacting fermions with a complicated and theoretically unknown dispersion law. Going further, starting from this hypothesis and invoking general considerations concerning the symmetry of crystals and using Fermi statistics, one might attempt to develop the quantum mechanics of the motion of such quasi-particles in external static electric and magnetic fields, in variable electromagnetic fields, including the effects of lattice vibrations, etc., and on the basis of such considerations make calculations of both the equilibrium statistical quantities for a metal (specific heat, magnetization, binding energy, etc.), as well as of the kinetic coefficients (electrical and thermal conductivity, galvanomagnetic effects, cyclotron resonance, etc.); in addition, by making a comparison of these results with experimental data one might attempt to establish the form of the energy spectrum of the quasi-particles and the shape of their Fermi surface. This is precisely the path which has been followed by I. M. Lifshitz and his coworkers [23] in a long series of papers† which develop a consistent phenomenological theory of metals on the basis of the hypothesis of a complicated character of the energy spectrum of the Fermi quasi-particles—the conduction electrons in metallic crystals. In these papers a detailed investigation is made of the various topological possibilities for Fermi surfaces, and in particular, a classification is introduced in them in which one distinguishes between open and closed surfaces. There is developed in detail a quasi-classical mechanics and quantum mechanics of Fermi particles with an arbitrary dispersion law. Lifshitz et al. introduced physically more reasonable definitions for the effective mass in terms of the geometrical characteristics of the Fermi surface. The concept of "holes" is more accurately described in terms of the nature of the dis-

persion law. Calculations are made of magnetic susceptibility (the de Haas—van Alphen effect, cf. below, Sec. 2), galvanomagnetic phenomena, electrical conductivity, cyclotron resonance, etc.*

These papers opened up a new and fruitful direction in the present electron theory of metals, in which one has by no means exhausted all the possibilities for further specific applications. However, in this phenomenological approach there still remains unsolved the most important question of the theory of metals, the origin of the complicated dispersion law, the form of this law, and the effect of electron interactions on the properties of the system of conduction electrons. The solution of these problems is the subject of the second direction along which people are thinking and developing the theory of metals at the present time.

Attempts to include interactions between the electrons have been made repeatedly and long ago,† but because of the complexity of this problem, the many-electron theory is still only in its initial stage of development. The difficulty in solving the many-electron problem consists in the fact that the energy of interaction of electrons cannot be regarded as small compared to the kinetic energy of the system. In fact, the energy of Coulomb repulsion of two electrons in a crystal, at the usual average distance between electrons of the order of the lattice constant ($a \sim 10^{-8}$ cm) is equal to $e^2/a \sim 10^{-20}/10^{-8} \sim 10^{-12}$ erg, while the Fermi energy $\zeta$ of an electron in a metal at normal densities ($n \sim 10^{22}$ cm$^{-3}$) is also of this same order of magnitude. Consequently, the ratio of these energies is $\sim 1$. Thus we are deprived of the possibility of introducing a small dimensionless parameter into the theory, which could then treat the electron interaction and use it for developing a scheme of computa-

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*This question is discussed in detail in the survey of V. L. Bonch-Bruevich.[22]

†A detailed description of the method and a bibliography of the papers are given in the survey paper of I. M. Lifshitz and M. I. Kaganov.[22]

*Landau[24] pointed out that in a system of Fermi quasi-particles it is not always consistent to neglect the interaction between quasi-particles. He therefore proposed a more consistent phenomenological treatment of the properties of fermion systems—the theory of a Fermi liquid. The basic assumption of this theory is that the interaction of fermions in a liquid is taken into account by the self-consistent field of the surrounding particles, so that the system energy can no longer be regarded as the sum of energies of individual fermions, but only as a functional of their distribution function. The energy of individual particles is then determined as the variational derivative of the energy density of the whole liquid in momentum space. Silin[25] treated in particular the problem of the extension of the whole scheme of the theory of Fermi liquids according to Landau (in its original form it had been developed for a system of fermions of the type of He³) to the case of conduction electrons in metals. The theory of a Fermi liquid has also confirmed all the conclusions ("statistical") of the band model, and has of course made some improvements in them.

†One of the first papers on the many-electron treatment of crystals is the paper by Heisenberg.[5] For the development of this work, cf. the survey papers by the author,[12, 26] Bonch-Bruevich,[22] and ter Haar,[27] which contain a detailed bibliography.

tion according to the usual theory of small perturbations.

In the general case, a system of N interacting electrons with a potential $U(\mathbf{r} - \mathbf{r}')$ is described by the Hamiltonian

$$\hat{H} = \sum_j \left[ \frac{\mathbf{p}_j^2}{2m_j} + U(\mathbf{r}_j) \right] + \frac{1}{2} \sum_{j \neq n} U(\mathbf{r}_j - \mathbf{r}_n), \qquad (1.4)$$

where $\mathbf{r}_j$ and $\mathbf{p}_j$ are the coordinates and momenta of the electrons, $U(\mathbf{r})$ is their potential energy in the field of the lattice. Thus, each particle moves in a field which is equal to the sum of the "external" field of the lattice and the field of interaction with all the other electrons $\sum_{n(\neq j)} U(\mathbf{r}_j - \mathbf{r}_n)$. It is just this last term which includes all the difficulties of the theory, since it introduces a non-additivity in the problem, as a result of which in the wave equation for determining the system wave function $\hat{H}\Psi = E\Psi$ (where E is the energy of the system) we cannot use the Fourier method for finding a solution in the form of a product of wave functions $\Psi(\mathbf{r})$ depending on the coordinates of just one particle. Therefore all of the efforts of theoretical physicists are devoted to the "struggle" with the double sum appearing in (1.4).

As has been pointed out by S. P. Shubin (cf. page 38 in the survey [26] and [12]), for the system of electrons in a crystal one can establish various properties which are insensitive to the specific form of the interaction between the particles. One can show that, independent of the form of interaction, the electrons in a crystal are not localized, that the energy spectrum must have a band character, and finally that the accelerating effect of a constant electric field is given in the general theory by the same formula as in the one-electron approximation. (For more details, cf. Sec. 5 in the survey[12]). However, these conclusions are so general that they cannot be used practically for calculating the specific quantities characterizing the properties of metals. Thus we again come to the need somehow to include the effects of the binary sum in (1.4). One method may be simply to drop this sum, or in a "softer" formulation to include it by some means in the first additive term on the right of (1.4). In this case we will be dealing with a one-electron theory with a "renormalized" additive potential. This is essentially the usual formulation of the band theory of Bloch and Peierls.[14] In quantum mechanics, however, there were already developed long ago more correct approximate methods for solving problems of many interacting microparticles. In studying the properties of many-electron atoms, it was made clear that one can with good accuracy introduce the concepts of individual states of electrons moving in a certain effective, self-consistent field produced by the aggregate action of the nuclei and all the other electrons

(the Hartree-Fock method*). Recently it has also been shown that nucleons in atomic nuclei, like electrons in the shells of atoms, form closed shells and behave as if they moved in a self-consistent field. Brueckner in a series of papers [29] has developed a new, more complete version of the self-consistent field method for nucleons in nuclei. Unlike the Hartree-Fock method, where one treats the motion of individual particles in the effective field of all (N−1) electrons, in the Brueckner method the interaction between pairs of particles is treated exactly, and one considers the motion of such pairs in the smoothed-out effective (self-consistent) field of the remaining (N−2) particles. A defect of these methods when applied to crystals, as compared to their use in problems concerning atoms and nuclei, is that whereas in the case of atoms and nuclei it is relatively simple to establish a direct comparison between the calculated energies of discrete levels and their experimental values obtained from spectroscopic experiments, in a crystal such a comparison is difficult. In the latter case one must, as a rule, compare with experiment the calculated microscopic characteristics: binding energy, specific heat, kinetic coefficients, in whose calculation one must make many intermediated simplifying assumptions, and we are left with an unknown error which is introduced by them into the final result.

During recent years, in the quantum theory of many particles, there has also been developed with success still another approximation method which is called the method of quasi-particles, or the method of collective variables (cf., for example,[22,30,27]). This method is especially suited for describing the motion of many-particle systems, and is related to the special class of their degrees of freedom which show a definite collective character and in which the individuality of the initial particles essentially disappears from view, since their interaction plays the main role. A typical example of this method is the description (in the linear harmonic approximation) of the thermal vibrations of crystal lattices by using phonons which determine the collective degrees of freedom of the ionic cores coupled to one another in the lattice. Another example of this method is the description of weak excitations (vibrations) of the spontaneous magnetization in a ferromagnet, by using ferromagnons or spin waves (which also are a sort of collective degree of freedom), caused by the exchange interaction of electron spins in crystals. In the general case in a complicated system of interacting quantum particles, all the degrees of freedom can be separated into individual ones (for example, electrons in an atom or a crystal moving in the self-consistent effective field) and

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*Cf., for example, paper[28]

into collective ones (such as phonons, ferromagnons, excitons in semiconductors, etc.).*

The method of collective variables is, however, unsuited to our problem of explaining the origin of the complicated dispersion law for conduction electrons in crystals of metallic type. This method "works" essentially for calculating branches in the energy spectrum of the system for those elementary excitations (quasi-particles) which are either small (so that the ratio of their number to the total number of degrees of freedom may be taken as a small dimensionless parameter in the theory) as is the case in the theory of spin waves in ferromagnets at low temperatures, or where the form of the interaction energy admits such a unitary coordinate transformation that the "undesirable terms" associated with the double sum in (1.4) disappear, as is the case in the harmonic approximation for the case of thermal vibrations of a crystal lattice (cf., for example, Sec. 105 in [31]). In the case of a system of interacting conduction electrons, however, both these conditions are not realized, since the number of quasi-particles in the system is equal to the number of particles one starts with, and the energy does not have a harmonic character.

The whole theory of collective behavior of systems of many particles† was used with success for metals and made it possible to improve our picture of the ground state of the conduction electrons and to introduce corrections associated with their dynamical correlations in calculating certain statistical and kinetic quantities for metals. These successes are associated with the plasma variant of the method of collective description of interactions. The experimental

and theoretical investigations of plasmas* have shown that electrons in plasmas exhibit a strong correlation, and they are therefore more similar to a liquid than to a gas. Because of their high mobility, the electrons have a strong screening action, so that the interaction potential between the charges in the plasma is not the Coulomb potential $\sim e^2/r$, but has the form of a screened potential: $\sim (e/r) e^{-r/\lambda_D}$, where $\lambda_D = (m \langle v^2 \rangle /12\pi n e^2)^{1/2}$ is the screening radius, or Debye length (here n is the density of particles in the plasma, $\langle v^2 \rangle$ is the mean squared velocity of the particles). In magnitude, $\lambda_D$ at normal densities of conduction electrons in metals $(n \sim 10^{23}\ cm^{-3})$ is of the order of the lattice constant $(\sim 10^{-8}\ cm)$. The second effect which occurs in the plasma is the nature of vibrations of the charges around their equilibrium positions and is called <u>plasma oscillation</u>. For these oscillations there exists a non-zero minimum frequency whose magnitude is equal to $\omega_{plas} = (4\pi n e^2/m)^{1/2}$. For ordinary densities of conduction electrons in metals $\omega_{plas}$ is $\sim 10^{16}\ sec^{-1}$. Thus the energy quanta for these vibrations (<u>plasmons</u>) are $\hbar\omega_{plas} \cong 10^{-11}\ erg \cong 10\ eV$. From the plasma model of a metal it follows that the conduction electrons can participate both in collective motion (plasma oscillations) as well as in individual motions. The Debye wavelength $\lambda_D$ is a convenient characteristic parameter of the theory in studying these two types of motions. For phenomena which are associated with distances larger than $\lambda_D$, the system behaves as "collective," as a gas of oscillators—plasmons. For phenomena with a characteristic distance smaller than $\lambda_D$, the system behaves like a system of quasi-individual particles which interact weakly via a screened potential. These conclusions are obtained both in the classical theory of plasma, as well as in the quantum theory. The latter, however, holds only under the condition that the Debye wavelength $\lambda_D$ is sufficiently large compared to the de Broglie wavelength of the corresponding particle $\lambda_B = \hbar/p$. For example, in his survey of the plasma model of metals, Pines [36] gives a detailed computation of the correlation corrections to the energy of an electron gas (i.e., corrections because of dynamical interaction) associated with the long-range and short-range (compared to $\lambda_D$) parts of the Coulomb repulsion of electrons with antiparallel spins. He also considers the effect of electron interaction on different physical properties of metals and the question of the excitation of plasma oscillations in connection with the characteristic energy losses of fast electrons passing through metals. Some of these "corrections"

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*In the survey of ter Haar[27] a simple example is given of such a splitting of degrees of freedom for a system of two particles of mass $m_1$ and $m_2$ with radius vectors $r_1$ and $r_2$, momenta $p_1$ and $p_2$, interacting through a potential $U(r_1-r_2)$ and placed in the gravitational field of acceleration g. The Hamiltonian of this system according to (1.4) has the form

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + m_1 g r_1 + m_2 g r_2 + U(r_1 - r_2).$$

If we introduce the relative coordinates of the particles r and the center of mass R and the conjugate momenta p and P, H takes the form

$$H = \frac{P^2}{2M} + M(gR) + \frac{p^2}{2\mu} + U(r), \quad M = m_1 + m_2, \quad \mu = \frac{m_1 m_2}{M},$$

$$R = \frac{m_1 r_1 + m_2 r_2}{M}, \quad r = r_1 - r_2.$$

This Hamiltonian describes the collective motion of the center of mass and the individual motion of the quasi-particles, with the effective (reduced) mass $\mu$, moving in the self-consistent effective field with the potential $U(r)$. This method is well known. For example, it is used in solving the problem of the simplest atomic system, the one-electron hydrogen atom (when one includes the nuclear motion), in treating excitons in superconductors as electron hole pairs, etc.

†Here we should mention the papers of Bohm and Pines,[32] Zubarev,[33] Zyryanov,[34] Tomonaga;[35] cf. also the survey of Pines[36] and ter Haar.[27]

*By a plasma we mean a gas of positively and negatively charged particles with a density of the order of $10^{12}\ cm^{-3}$, which is of great importance in phenomena of electrical discharges, thermonuclear processes, etc. The electron gas in a metal is distinguished by the fact that in it the positive charges form a crystal lattice, while the density of the electrons reaches very large values, $\sim 10^{23}\ cm^{-3}$.

will be discussed by us later in Secs. 2 and 3 in presenting specific results concerning the description of magnetic properties of metals and their electrical conductivity.

The plasma model introduced a fresh point of view in the problems of metals and made it possible, to a certain extent, to overcome the limitations of band theory in its one-electron form. However, it was not free of model simplifications, so that one cannot regard the plasma treatment of a metal as consistent and complete and suitable for a rigorous description of the properties of strongly interacting systems of conduction electrons, and certainly not for explaining the origin of the complicated dispersion law, the form of the Fermi surface, etc. The most annoying and weak point of the plasma theory of metals is the fact that for actual densities of conduction electrons in real metals, the characteristic plasma Debye wavelength $\lambda_D$ is comparable in order of magnitude with the de Broglie wavelength $\lambda_B$ for electrons at the Fermi surface. One therefore cannot take over to the case of electrical conduction in metals the conclusions of the classical plasma theory. In regions of space with linear dimensions of the order of $\lambda_D \sim \lambda_B$ it is already necessary explicitly to take into account specific quantum effects (of the type of diffraction of electron waves, etc.). Therefore the conclusions of plasma theory are closer to the real situation in metals in the case of heavy metals, where the condition $\lambda_D > \lambda_B$ is already more or less satisfied. Just because of this fact, the plasma model gives fairly good results for those effects for which the characteristic wavelength $l$ satisfies the condition $l > \lambda_D$ (for example, the scattering of sound waves with wavelength $\lambda > \lambda_D$, etc.).

In recent years there has been begun a very intensive development of rigorous quantum-mechanical methods for treating problems of solid state physics. In this connection we should make one important remark concerning the features of solids (including metals) as systems of many interacting quantum particles.[26] These bodies have a very large number of degrees of freedom ($\sim 10^{23}$), and consequently their energy spectrum has an unusual richness in levels. From quantum statistics it is well known (cf., for example, Secs. 5, 7 in [37]) that the average spacing between neighboring levels $D(E)$ is given by the formula

$$D(E) \simeq e^{-S(E)},$$

where $S(E)$ is the entropy of the system, and is proportional to the number of particles. Therefore the distance between levels is a negligibly small quantity $\exp(-10^{23})$. Because of this superhigh density of levels, it follows that condensed bodies are not in rigorously stationary states. This is due first of all to the fact that the energy levels of the system always suffer broadening because of unavoidable interactions with the surrounding medium. This broadening is always

greater than the distance between levels given above. Secondly, there is still the natural quantum broadening of energy levels associated with the uncertainty relation for energy and time: $\Delta E \, \Delta t \sim \hbar$. These circumstances lead one to the conclusion that in a microscopic treatment of the physical properties of condensed macrobodies one should, as a rule, use not quantum mechanics, but quantum statistics; one should not concern oneself with determining the eigenfunctions of a quantum mechanical system and its energy spectrum, but rather with finding the statistical operator or the density matrix,[37] which are the quantum mechanical analogues of the distribution function of classical statistics. This is precisely the direction in which the development of the most consistent quantum treatment of the problems of solid state theory is going at present.* Before presenting the results of the application of quantum statistical methods to the problems of metals which we are interested in, let us first, following Herring,[41] consider the purely qualitative explanation of the influence of electron interactions on the nature of the distribution of the electrons over quasimomenta, which in the non-interacting system of fermions has the form of a Fermi step-function (cf. Fig. 1). If we start from the notion that initially, in the interacting system, the distribution function had such a step shape, then when we include the electrostatic repulsion of electrons they can no longer remain permanently in states with a definite value of the vector $\mathbf{k}$. Because of the action of the forces between the particles, they experience an acceleration and therefore will at some time move faster than was assumed in the case of the absence of interaction. Because of this the distribution $f(\mathbf{k})$ "below" the Fermi surface will now be less than unity and "above" it it will be different from zero. At first glance one might think that the Fermi step function (cf. Fig. 1) would, as a consequence, get smeared out completely (just as should occur for an ideal Fermi gas at temperatures which are considerably above the degeneracy temperature, T $\gg \zeta/k$[14]).

However, as has been shown by theoretical calculations using the new quantum-statistical methods (density matrix, Green's function, etc.), such a smearing may not occur, or it may be relatively small. Therefore, in real many-electron systems with arbitrary interactions, in some sense one retains the concept of a Fermi surface as the surface at which the distribution function experiences a sharp, discontinuous change. Consequently, also in the case of a system of interacting particles there are excited states of the many-electron system which, although they are somewhat changed in form, still in the strict

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*Aside from the surveys previously mentioned,[12, 26, 27] in which some use is made of the density matrix, we should also mention special surveys devoted to this problem.[38-40]

sense can be described as having holes in certain states just below the Fermi surface and excited electrons immediately above the Fermi surface. However, this analogy of the states of a many-electron system with the states of an ideal gas of Fermi particles is valid only for states in the immediate vicinity of the Fermi surface. The point is that if we imagine the states of a system of interacting particles as having an excited electron or a hole in states very remote from the Fermi surface, then the electron-electron "collisions" will be so intense and the excited electron or hole will shift so rapidly into other "momentum" states that the initial states (which are very far from the Fermi surface) cannot at all be regarded as stationary. However, as the excited states approach the Fermi surface, the collisions become very rare and such initial states differ very little from stationary states. Thus, in the space of quasi-momenta there will exist a surface such that when one passes over it the probability of occupation of the possible one-electron states suffers a jump, and in the immediate neighborhood of which there may exist quasi-particles of the type of electron and hole which can transport current, be accelerated in an external field, etc. This surface is the Fermi surface. It exists in a metal and does not exist in an insulator in which the energy of the ground state is separated by a gap from the energy of the first excited states. However, a Fermi surface does not exist for every system of fermions. For example, as pointed out by Luttinger, [42] a system of interacting deuterium atoms, subjected to Fermi statistics, in its ground state forms a molecular crystal of $D_2$ molecules and shows no traces of a Fermi surface in its distribution of particles over momenta. Therefore the existence of a Fermi surface seems to depend on the nature of the forces between the fermions. At this point there is still no complete understanding of the theory. For example, Luttinger [42] investigated a case where the forces between particles can be expanded in perturbation series (convergent in the usual sense). However, the question still remains whether the system of conduction electrons in a metal satisfies this requirement. One can only again appeal to the good agreement with experiment of the numerous results of the band theory and the phenomenological theory of fermions. Mathematically, quantum mechanical treatments at present are as a rule carried out using the Green's function method (cf., for example, the surveys [43-45]).* This method is analogous to the well-known method of the Green's function in mathematical physics, where this function plays an auxiliary

*The Green's function method was first developed for problems of the quantum theory of fields,[16,47] from which it was borrowed for solving problems of many interacting particles in the non-relativistic quantum theory of condensed bodies. The first papers where this method was applied for systems of interacting fermions are due to Midgal and Bonch-Bruevich[48] (cf. also the collection of translations[49]).



FIG. 4. Schematic picture of the distribution function f(k) for a system of interacting fermions ($0 < \Delta f(k_0) \leqslant 1$).
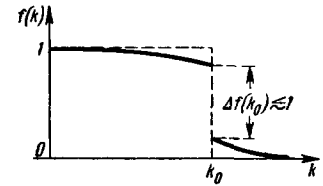
role in finding the solution of differential equations. Of especial interest is the so-called temperature Green's function, [46] by means of which one can very conveniently define the statistical characteristics of quantum systems of many particles over a wide range of temperatures. By means of temperature Green's functions, for the case of a system of interacting electrons, one can find the distribution function in the following general form:

$$f(\mathbf{k},\sigma^z)= \int_{-\infty}^{\infty} \frac{dE}{e^{E/kT}+1} \frac{1}{\pi} \frac{\Gamma_{\mathbf{k}\sigma^z}(E)}{[E-\tilde{\varepsilon}(\mathbf{k},\,\sigma^z)+\mathfrak{M}_{\mathbf{k}\sigma^z}(E)+\zeta]^2+\Gamma^2_{\mathbf{k}\sigma^z}(E)},$$ (1.5)

where k is the Boltzmann constant, $\tilde{\varepsilon}(\mathbf{k},\sigma^z)$ is the renormalized energy of the quasi-particle, $\mathfrak{M}_{\mathbf{k}\sigma^z}$ is a mass operator taking into account the interaction between particles, and $\Gamma_{\mathbf{k}\sigma^z}$ is a quantity describing the damping of quasi-particles caused by all of their interactions (among themselves and with other sources of field), $\zeta$ is the chemical potential of the system, i.e., the Fermi energy. If we neglect damping and the mass operator, expression (1.5) goes over into the usual Fermi distribution function for a gas of non-interacting fermions, with a dispersion law

$$\tilde{\varepsilon}(\mathbf{k},\sigma^z):f_0(\mathbf{k},\sigma^z)= \frac{1}{e^{\frac{\tilde{\varepsilon}(\mathbf{k}\sigma^z)}{kT}}+1}.$$

As was shown, for example, in [42], even when one includes the quantity $\mathfrak{M}$ in $\Gamma$, it turns out that there is an abrupt change in the distribution function; the surface where this occurs is the Fermi surface for the system of interacting particles. There is every reason to believe that this jump differs little from unity and that the distribution function has the form shown schematically in Fig. 4. One can also show that the volume in k space, bounded by the surface of discontinuity of the distribution function for the system of interacting fermions, is equal to the volume bounded by the Fermi surface of an ideal gas of fermions. Thus the interaction can deform the Fermi surface, but it cannot change the volume bounded by it. In the isotropic case the Fermi surface preserves its spherical form even when interactions are included. These computations can also be generalized to the case where the system of interacting fermions is placed in the periodic field of an ionic lattice. Here one can have three cases: one of them corresponds to a metal, where the Fermi surface lies within an energy band, and the two others to the case of semiconductor or insulator where there is a completely filled, or a completely empty band. Thus one can in a certain sense say that the many-electron theory has already

given a basis for band theory in its phenomenological form. One should also mention that the phenomenological theory of the Fermi liquid due to Landau[24] also finds its justification in the microscopic quantum-statistical theory of many particles (cf., for example, the appendix to the survey [24b]).

So far it has been assumed that the metallic crystal consists of a system of collectivized conduction electrons (arising from the valence electrons of the isolated atoms) and a lattice of ionic cores with closed electron shells which are in s-states, i.e., having completely compensated orbital and spin-angular momenta (mechanical and magnetic). This is the case for the so-called normal or non-transition metals. In addition there also exist metals made up of atoms of the transition elements, which have incomplete inner d- or f-shells of electrons. These metals are called transition metals. The electrons of the incomplete shells, when they condense into a crystal, take an active part in the formation of the collective electron properties, and thus introduce many special features into the physical properties of transition metals as compared with the properties of non-transition metals. Here one must also distinguish transition metals made up of atoms with incomplete d-shells (metals of the iron group, with an incomplete 3d-shell, the palladium group with an incomplete 4d-shell, and the platinum group with an incomplete 5d-shell) and those with incomplete f-shells (the rare-earth metals with an incomplete 4f-shell and the actinide metals with an incomplete 5f-shell), i.e., we must distinguish between d-metals and f-metals. This difference is caused by the difference in effective radii of these shells relative to the distance between lattice sites—between nearest neighbors in the crystal. In the d-metals, the d-shells overlap considerably for neighboring sites, and this results in a collectivization of these electrons which, together with the former valence electrons, form a complex system of conduction electrons for the transition d-metals. These metals have a high density of conduction electrons which manifests itself, for example, in a high value of the electronic specific heat,[19] a more complicated distribution of electron density in space, and also a more complicated form of the Fermi surface and the dispersion law. In them the conduction electrons occurring from collectivization of the former d-shells also have an increased value of their effective mass (in the band picture, the d-electrons correspond to a very narrow energy band in the spectrum). But in the case of the f-metals the radii of the f-shells are so small that the corresponding electron clouds in crystals are almost completely non-overlapping, and therefore the incomplete f-shells are practically bound tightly to the ion cores. Thus in the f-transition metals these cores have an unfilled electron shell with non-zero spin and orbital mechanical and magnetic angular momenta. This fact also results in many specific fea-

tures of the electronic properties of the f-metals. The above description shows clearly that the problem of the transition metals has a significance of its own in the general problem of the theory of the metallic state of matter (for more details, cf. the survey[50]).

Thus we can cite certain accomplishments of the treatment of the general properties of the system of conduction electrons in metals. This system is an aggregate of interacting fermions. The ground state of the system has a large zero-point energy (the Fermi energy). In the space of quasi-momenta there is a surface of discontinuity of the distribution function—the Fermi surface. The energy spectrum of this system is continuous.* Excitations of individual type have the character of excited electrons and holes (because of the complicated dispersion law, these excitations also have a more complicated character than was assumed in the elementary band model). In addition, in the excitation spectrum there may also be Bose branches associated with plasma oscillations of the electron system and also with vibrations of the spin system (spin waves).† As an illustration, we now consider qualitatively the explanation of two typical electronic properties of metals: magnetic properties (Sec. 2) and electrical conductivity (Sec. 3).

## 2. MAGNETIC PROPERTIES OF METALS

The system of conduction electrons and the lattice of ion cores of a crystal, like any system of moving electrically charged particles, has definite magnetic properties. In this system, as in any magnet, there exist together two magnetic "tendencies," dia- and paramagnetic. The first is associated with the induced action of external electromagnetic fields on the molecular currents in the material, which produce a diamagnetic moment in the body which is directed opposite to the field producing it (Lenz's law). The paramagnetic tendency is associated with the orientation effect of external magnetic fields on the intrinsic magnetic moments of the microparticles of the matter. In addition, the internal interactions between the particles of the system have an essential influence on the magnetic properties. Thus the carriers of magnetism in metals as in other bodies are

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*In many metals, however, because of the interaction of conduction electrons with the lattice vibrations (phonons), effective attractive forces appear between them which produce a gap in the energy spectrum and lead to the phenomenon of superconductivity. A more detailed treatment of this question would go beyond the realm of the present survey (cf., for example, the surveys[51,52] or the monograph[53]).

†In principle one can also imagine the existence of Bose branches in the spectrum of collectivized electrons of a crystal with excitations possessing a charge (in contrast to the uncharged excitations of the type of excitons, ferromagnons, etc.). However, so far in experiment such branches of the electron spectrum have not been observed. (Cf., concerning this question, paper[54]).

the electrons and the atomic nuclei. Nuclei and electrons differ markedly in the magnitude of their magnetism. This is caused by the fact that the quanta of electronic magnetism (the Bohr magneton $\mu_B$ = $e\hbar/2mc \cong 10^{-20}$ cgs emu) and of nuclear magnetism (the nuclear magneton $\mu_n$ = $e\hbar/2Mc \cong 10^{-23}$ cgs emu; here M is the mass of the nucleon which is equal to 1836.5 times the electron mass m) differ by almost a factor of 2000 ($\mu_B/\mu_n$ = 1836.5). We therefore consider only the stronger magnetism of the electrons.* Here we should distinguish between the magnetism of the conduction electrons and the ion cores, and also between the cases of transition and non-transition metals.

A. Magnetic properties of conduction electrons and ion cores in non-transition metals. As is well known, the electron has an intrinsic magnetic moment associated with its spin. The magnitude of this moment is $\sqrt{3}\,\mu_B$, and it may be directed only in two ways relative to the axis of quantization—the direction of the external magnetic field: $\pm\mu_B$. In addition, the electrons in a metal carry out "orbital" motions associated with a quasi-momentum k. The external field H will change this motion, producing a Larmor precession of the electrons whose magnetic moment causes a diamagnetic effect. The quantum nature of the electron, primarily the Fermi character of its energy spectrum, results in particular para- and diamagnetic effects in metals. Generally speaking, these effects always exist together, and they should strictly speaking be treated simultaneously. But since, as a rule, the paramagnetic effect is greater than the diamagnetic, one can approximately treat them separately.

A1. Spin paramagnetism of the conduction electrons (Pauli [20]). The system of conduction electrons in the approximation of the ideal Fermi gas, in its ground state has no resultant spin magnetic moment, since all the unit cells in the quasi-momentum space are occupied by two electrons with opposite spin projections. This is one of the examples of the fact that the Pauli principle (the antisymmetric character of the wave function) in systems of fermions leads to a fundamental dependence of their energy on their magnetic

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*Naturally the magnetic properties of systems of atomic nuclei in metals have various specific features associated with the interaction of conduction electrons and nuclei of the type of hyperfine structure for isolated atoms. The deviation of the wave function of the conduction electrons from zero in the region occupied by the nuclei makes this interaction (the contact Fermi interaction) very important and is the cause of specific features of nuclear magnetic properties in metals. Concerning this problem, cf. the surveys[99, 100]. The magnetic interaction between conduction electrons and atomic nuclei in ferro- and antiferromagnetic metals has taken on special interest in connection with the discovery of the Mössbauer effect,[101] which gives the possibility of measuring the magnitude and sign of the effective magnetic field, acting on a nucleus, produced by the electron system in the crystal. This problem is discussed in more detail, for example, in the survey[50] and also in[105].
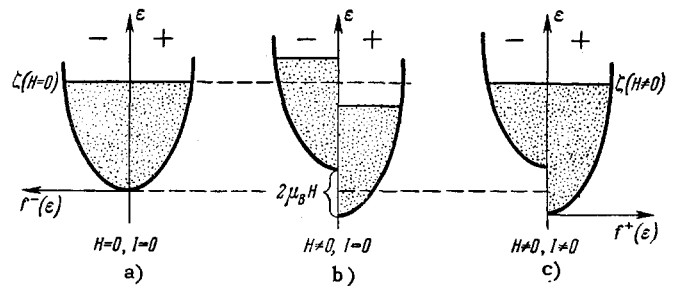


FIG. 5. Distribution functions of electrons with different spin projections, omitting exchange and correlation corrections. a) in the absence of magnetic field (H = 0); b) in the presence of a magnetic field in the unmagnetized state (H $\neq$ 0, I = 0); c) in the magnetized state (H $\neq$ 0, I $\neq$ 0).

properties, even when one does not include the magnetic or the electrical dynamic interaction of the fermions. This is precisely the cause of the specific magnetic properties of metals. In the paper referred to earlier,[4] Frenkel gave a rigorous, but at the same time, simple derivation of the paramagnetic spin susceptibility of an ideal gas of conduction electrons. In the magnetization of such a gas one expends a large energy, since the field must shift electrons from completely occupied levels below the Fermi energy to free levels which lie above this energy, for each change in sign of a spin projection. Before the turning on of the field, the distribution functions* $f^{\pm}(\epsilon)$ for the electrons with different spin projections do not differ from one another (Fig. 5). After turning on the field, there occurs a lifting of the spin degeneracy and the functions $f^{+}(\epsilon)$ and $f^{-}(\epsilon)$ "shift" relative to one another by an amount $2\mu_B H$ along the energy axis (i.e., by the amount of energy which is required to change the sign of a spin projection in the field to its reverse). This shift in the levels destroys the equality of the energies for the states with opposite projections of the spin, and therefore destroys the equal population of states with opposite projections, so that it no longer corresponds to a minimum in the energy of the system. Electrons shift over from the "raised" distribution to the "lowered" one, so that one again has a common Fermi surface (cf. Fig. 5), but in doing this a magnetization appears in the fermion gas. If we neglect the change in the distribution function f($\epsilon$) over the energy interval $\sim \mu_B H$ (this is justified for fields $\lesssim 10^4$ Oe, since the energy $\mu_B H$ is then equal to $\sim 10^{-20} \times 10^4 \sim 10^{-16}$ erg, and consequently is $10^4$–$10^5$ times smaller than the Fermi energy $\sim 10^{-12}$–$10^{-11}$ erg), the magnetization produced by the field will be equal to

$$I \sim \{f^{+}(\zeta) - [-f^{-}(\zeta)]\}\,\mu_B H \mu_B \approx f(\zeta)\,\mu_B^2 H \qquad (2.1)$$

and consequently the paramagnetic susceptibility will be

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*We are speaking here of the distribution function in energy f($\epsilon$), and not with respect to wave vector f(k). In the case of a quadratic dispersion law, it has the form: f($\epsilon$) = $4\pi/h^3$ $(2m)^{3/2} \times \epsilon^{1/2}$ for $\epsilon \leqslant \zeta$, and f($\epsilon$) = 0 for $\epsilon \geqslant \zeta$ (cf. Fig. 1b).

$$\chi_{pm(el)} \sim \mu_B^2 f(\zeta), \qquad (2.2)$$

i.e., in first approximation it will be determined entirely by the electron levels in the neighborhood of the Fermi surface. One can also show that in this same approximation $\chi_{pm(el)}$ is independent of the temperature T. In fact, because of the high degeneracy of the electron gas, only the thermally excited electrons will participate in the paramagnetism, and their density in first approximation is determined by the ratio of the temperature T to the degeneration temperature of the Fermi gas $\theta = \zeta/k$, i.e., $n_T = n(kT/\zeta)$. Each electron of the total number $n_T$ will behave like a classical particle with magnetic moment $\mu_B$, i.e., it will be subject to the Curie law [8] for susceptibility: $\chi = n_T \mu_B^2 / 3kT$. Replacing $n_T$ by its expression written above, we find for the susceptibility of the Pauli magnetism of a Fermi gas

$$\chi_{pm(el)} \sim \frac{n\mu_B^2}{3\zeta} . \qquad (2.3)$$

From this we see that $\chi_{pm(el)}$ in this approximation actually is independent of T. A more exact calculation shows that $\chi_{pm(el)}$ depends weakly on T. Including the interaction changes somewhat the value of $\chi_{pm(el)}$. Thus, for example, Hartree-Fock exchange corrections to the energy increase the susceptibility $\chi_{pm(el)}$, since they reduce the Fermi energy. On the other hand, Coulomb correlation corrections raise $\chi_{pm(el)}$ and therefore partially compensate the effect of exchange corrections. For example, for alkali metals we give in Table I values of $\chi_{pm(el)}$ calculated for an ideal Fermi gas and with corrections for correlation. We also give values of the mean distance between "neighboring" electrons $r_s$ in units of the Bohr radius. From Table I we see that the compensation of "corrections" for correlation improves with increasing $r_s$.* Experiments for determining $\chi_{pm}$ (by the method of paramagnetic resonance) for example, for lithium [55] give a value $\chi_{pm} = (2.0 \pm 0.3) \times 10^{-6}$ (at room temperature), which is in good agreement with the calculated theoretical value $1.87 \times 10^{-6}$. The many-electron theory of fermion systems [42] and the theory of the Fermi liquid [24b] also give correlation corrections like the plasma model.

**A2. Orbital diamagnetism of conduction electrons** (Landau [21]). From classical electrodynamics it is known that a magnetic field H directed along the z axis will cause an electron moving in this field to undergo a precession with a Larmor frequency $\omega_H$ = eH/mc. The circular precession around the z axis can be resolved into a sum of two mutually perpendicular linear periodic motions along the x and y axes. As was first shown by Landau, [21] in quantum mechanics these motions are quantized according to the law for a linear harmonic oscillator, with the discrete energy spectrum

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*In this connection, see the note in Sec. 1 concerning the domain of validity of the plasma model.

**Table I. Paramagnetism of conduction electrons in alkali metals (for 0°K) [36]**

| Metal | $r_s$ | $\chi_{pm(el)}^{id} \times 10^6$ | $\chi_{pm(el)}^{corr} \times 10^6$ |
|---|---|---|---|
| Li | 3.22 | 1.17 | 1.90 |
| Na | 3.96 | 0.64 | 0.85 |
| K | 4.87 | 0.48 | 0.60 |
| Rb | 5.18 | 0.44 | 0.52 |
| Cs | 5.57 | 0.38 | 0.43 |

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega_H = \frac{eh}{mc} H \left( n + \frac{1}{2} \right) = 2\mu_B H \left( n + \frac{1}{2} \right), \qquad (2.4)$$

where $n = 1, 2, 3, 4 \ldots$ are the quantum numbers of the oscillators. The motion along the z axis is not quantized, but remains free with a continuous energy spectrum $p_z^2/2m$. Knowing the energy spectrum of the electron in a magnetic field, one can by using the usual formulas of statistical physics [8b] calculate the diamagnetic susceptibility $\chi_{dm(el)}$ of the Fermi gas of electrons. It is equal to one-third of its paramagnetic susceptibility (2.3). In the band theory, where one takes into account the effect of the ionic lattice, the expression for $\chi_{dm(el)}$ is more complicated. In particular, the correction to $\chi_{dm(el)}$ depends essentially on the shape (curvature) of the Fermi surface and may have either a positive or a negative sign, or may be fundamentally anisotropic. In Table II we give a comparison of the theoretically computed values of $\chi_{dm(el)}$, $\chi_{pm(el)}$, and $\chi_{dm(ion)}$ of the ionic cores with experimental measurements of the total susceptibility of alkali metals at room temperature. From Table II we see that the theory gives too high (in absolute value) values for the Landau diamagnetism. This presumably indicates the crudeness of the theory for this purpose.

**A3. The de Haas–van Alphen effect.** At low temperatures there is a very interesting phenomenon, related to the diamagnetism of the conduction electrons in metals. This phenomenon consists of a periodic (oscillatory) dependence of the magnetic susceptibility of a large number of metals (beryllium, bismuth, zinc, tin, magnesium, indium, cadmium, gallium, etc.), discovered by de Haas and van Alphen. [56] This effect is a

**Table II. Diamagnetic susceptibility of conduction electrons of alkali metals (at room temperature)**

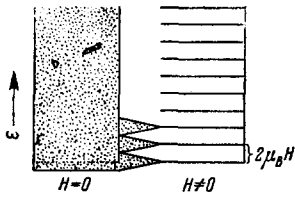| Metal | $\chi_{pm(el)} \times 10^6$ | $\chi_{dm(el)} \times 10^6$ | $\chi_{dm(ion)} \times 10^6$ | $\chi_{tot}^{th} \times 10^6$ | $\chi_{exp} \times 10^6$ |
|---|---|---|---|---|---|
| Li | 1.87 | −0.18 | −0.05 | 1.64 | 1.97 − 2.11 |
| Na | 0.84 | −0.25 | −0.18 | 0.41 | 0.65 − 0.74 |
| K | 0.59 | −0.21 | −0.31 | 0.07 | 0.36 − 0.49 |
| Rb | 0.51 | −0.21 | −0.32 | −0.02 | 0.11 − 0.33 |
| Cs | 0.42 | −0.21 | −0.42 | −0.21 | −0.20 − 0.44 |

FIG. 6. Schematic diagram of the quantization of the energy of conduction electrons in an external magnetic field.

purely quantum effect (like all the equilibrium magnetic properties of materials [8b]) and is caused primarily by the high degeneracy of the conduction electrons, and secondly by the effect of quantization of the energy of these electrons in a magnetic field [cf. (2.4)]. In the absence of a magnetic field, the energy spectrum corresponding to the progressive motion of conduction electrons in the $(x, y)$ plane is continuous (cf. Fig. 6). When the external field H along the z axis is turned on, the spectrum for these degrees of freedom, according to (2.4), splits into narrow, discrete bands of width $\Delta E = 2\mu_B H [(n + \frac{1}{2} + 1) - (n + \frac{1}{2})] = 2\mu_B H$, each of which is "squeezed" down into one discrete level, which is $2\mu_B H$-fold degenerate. For a given value of the field H, the Fermi level falls on one of these discrete levels. If we now change the magnitude of the field, we will change the degree of degeneracy of the discrete levels, i.e., they will be compressed from bands of another size $2\mu_B H'$, and the Fermi level will then jump periodically from one level to another. This should lead to oscillatory effects for all the equilibrium and kinetic characteristics of conduction electrons when we change the value of the magnetic field. With increasing temperature, when the Fermi step begins to get smeared out, the oscillations will diminish. Lifshitz and Kosevich, [57] within the framework of the phenomenological theory of metals with an arbitrary dispersion law for fermions, have worked out a consistent and detailed theory of the de Haas—van Alphen effect. The most important conclusion of this theory is the establishment of a regularity in the relation between the oscillation period $\Delta(1/H)$ (expressed in units of the reciprocal field $1/H$) and the extremal cross sectional area $S_m$ of the Fermi surface perpendicular to the field H. Thus detailed investigations of the de Haas —van Alphen effect in single crystals enable one to reproduce the shape of the Fermi surface and to determine the velocities of electrons at the surface, etc. Comparison of the theory and experiment in static fields of the order of $10^3$—$10^4$ Oe has shown that in metals, in which one observes most clearly the effect of oscillation of the magnetic moment, there exist anomalous groups of small numbers of electrons (holes) with small values of the effective mass. A further improvement and extension of the experiments and theoretical calculations of this effect is an important problem for the further development of the quantum theory of metals. It should be mentioned that Luttinger, within the framework of the many-electron calculations using the Green's function method, has shown [58] that in a magnetic field one obtains oscilla-

tory effects in period and amplitude of the same type as in the calculation of Lifshitz and Kosevich, [57] but that the phases of the oscillations are more complex in nature.

A4. Diamagnetism of ion cores with closed shells. In the case of non-transition metals, the electronic shell of the ion cores of metal crystals are in an S-state with completely compensated orbital and spin magnetic moments. Therefore, the ion cores can only make a diamagnetic contribution to the electron magnetism of the crystal (cf., for example, Table II). A calculation of the diamagnetic susceptibility of ion cores is usually carried out by the method of the self-consistent field for isolated atoms. In principle, of course, one should in crystals include the mutual polarization of the ion cores and the influence on the charge distribution in them of the conduction electrons.

B. Magnetic properties of conduction electrons and ion cores of transition metals. [50] As already pointed out at the end of Sec. 1, transition metals should have specific electronic properties since in them in the formation of the electron system an important part is played not only by the former valence electrons of the isolated atoms, but also by the electrons of the unfilled d- and f-shells. Then, as already pointed out above, in the case of the d-transition metals there is a significant increase in the density of conduction electrons because of the active participation in this system of the former d-electrons, so that the magnetic properties of these metals are determined by changes in the system of conduction electrons. In the case of the f-transition metals, the f-electrons are practically not collectivized and remain rigidly bound to the ion cores, so that the magnetic properties of this class of transition metals will essentially be determined by changes in the structure of the ion cores, by their strong paramagnetism. Before proceeding to calculate the main types of magnetic states realized in transition metals, let us consider the general question of the possible magnetic properties of a system of interacting fermions. We have seen on the example of an ideal gas of Fermi particles that there is a very strong "antimagnetic" tendency, since the ground state of such a gas has no magnetic moment (because complete compensation of the spin moments occurs within the volume bounded by the Fermi surface). If, however, we include exchange interaction between the conduction electrons, then, as first shown by J. I. Frenkel, [4] there also appears a tendency which is favorable to the magnetization of the Fermi gas. In the approximation of the Hartree-Fock method, where we include this interaction, the energy (expressed in Rydbergs) of unit volume of the electron gas, for the unmagnetized state is equal to

$$E_{(I=0)} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s}. \tag{2.5}$$

The first term in (2.5) is the kinetic energy (Fermi

energy), and the second term is the exchange energy. For the completely magnetized state the energy is

$$E_{(I=I_{max})} = \frac{3.52}{r_s^2} - \frac{1.156}{r_s}. \qquad (2.6)$$

From a comparison of (2.5) and (2.6) one can easily determine that for $r_s \geq 5.45$ a gas of Fermi particles should be magnetized to saturation, i.e., should be ferromagnetic. However, for example, in the case of the alkali metal cesium, where $r_s = 5.57$, ferromagnetism is not observed. This disagreement with experiment, as was first pointed out by Wigner,[59] is explained by the fact that, in the expressions given for the energy of a Fermi gas, the interaction has not been included accurately enough. The difference between the exact energy and expressions (2.5) or (2.6) is called the correlation energy. This energy also is favorable to the unmagnetized state of the electron system. In all the non-transition metals the exchange energy cannot overcome this demagnetizing tendency of the Fermi energy and the correlation energy, so that in these metals one does not observe the phenomena of ferro- and antiferromagnetism. But in the case of the transition metals, where we have a high density of electron levels at the Fermi surface, narrow energy bands and large effective masses of electrons, the situation may become more favorable for the exchange energy, and the electron system may achieve a spontaneous magnetic moment, i.e., we may have the case of ferromagnetism (or antiferromagnetism). These concepts are the basis of the so-called collective electron model in the theory of ferromagnetism. The most up-to-date treatment of this model is given in the paper of Shimizu[60] (cf. also the survey [50]).

B1. Spin paramagnetism of collectivized electrons in transition d-metals. If in the system of collectivized electrons of d-metals the magnetizing tendency of the exchange interaction is completely suppressed, the metal will be in a paramagnetic state (if, of course, the spin paramagnetism of the electrons in the crystal exceeds the sum of the diamagnetic Landau effect and the diamagnetism of the ionic cores with closed shells). The electron paramagnetism of the transition d-metals as a rule is much greater, for example, than the paramagnetism of the alkali metals. This can be understood even from formula (2.2) from which we see that $\chi_{pm}$ is proportional to the density of electron levels at the Fermi surface. The same quantity in the transition d-metals is considerably greater than in the non-transition alkali metals, which also explains the increase in $\chi_{pm}$ for the first group. This conclusion is confirmed by the fact that for the d-metals we have a much higher value for the electron specific heat than in alkali metals, and the specific heat is also proportional to the electron density at the Fermi surface. (This problem is discussed in more detail in [61] and also in the survey [50]).

B2. States of atomic magnetic order in transition d-metals and alloys. In those cases where the ex-

change interaction in a system of former d-electrons, subjected to considerable collectivization in a crystal, "conquers" the antimagnetic tendency of the Fermi energy and the correlation effects, in the low-temperature region (from 0°K up to the critical Curie or Neel point), an atomic magnetic order may appear. This can be either ferromagnetism, in which case the system has a non-zero resultant magnetic moment (spontaneous magnetization), or antiferromagnetism, where there is no resulting moment, but there is a spatially ordered distribution of electrons with opposite projections of their spin magnetic moments.* Experiments show that of the 24 transition d-elements (iron, palladium, and platinum groups) only in five metals of the iron group does one have a state with atomic magnetic order: ferromagnetic in iron, cobalt, and nickel, and antiferromagnetic in chromium and manganese. In addition, there are a large number of alloys of these metals which possess ferro- or antiferromagnetism. Ferro- and antiferromagnets of this group of materials have characteristic features. Let us mention some of the most typical. First, the average atomic magnetic moments in these materials† differ considerably in magnitude from the values of the magnetic moments of isolated atoms and ions of these elements, or from the moments of these ions in non-metallic compounds. In addition the average atomic moments are fractional (in units of $\mu_B$); for example in the case of iron $\mu_{at. Fe} = 2.22 \mu_B$, for nickel $\mu_{at. Ni} = 0.61$, etc. It is also important to point out that the ferro- and antiferromagnetism of the d-metals and alloys as a rule has a purely spin character and that the orbital mo-

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*Landau[37] pointed out that, in the general case, the symmetry of the crystal determines not only the symmetry of the scalar function $\rho(r)$ for the electron density, but also the symmetry of the time-averaged vector function for the microdensity of electric current, $j(r)$. All bodies can be divided into two classes: $j \neq 0$ and $j = 0$. For $j \neq 0$ the integral of $j$ over a unit cell of the crystal, $\int j \, d\tau$ is equal to 0, for otherwise there would appear a large positive energy of the magnetic field of the microcurrents which would appear within the volume of a body and this is thermodynamically unfavorable. However, in bodies with $j \neq 0$ there can arise a non-zero macroscopic magnetic moment $M = \int r \times j \, d\tau \neq 0$. Therefore bodies with $j \neq 0$ can in turn be divided into two classes: those with $M \neq 0$ (ferromagnets) and those with $M = 0$ (antiferromagnets). The symmetry of the vector function $j(r)$ can be regarded as a symmetry in the orientations of the atomic magnetic moments. In diamagnets (at $H = 0$) $j \equiv 0$, and consequently magnetic moments are absent. In diamagnetic materials, moments cannot occur in general, while in paramagnetic materials the magnetic moments (currents) are oriented in an irregular fashion and are equal to zero on a time average. In bodies with a "magnetic atomic structure" (i.e., $j \neq 0$) the moments $\int r \times j \, d\tau$ in each unit cell of the crystal may be different from zero for ferromagnets and equal to zero for antiferromagnets.

†By the average atomic magnetic moment of a ferromagnet we mean the ratio of the value of the spontaneous magnetization (extrapolated to the value corresponding to 0° K) to the number of magnetically active atoms per unit volume. In the case of antiferromagnets, the same definition applies to the spontaneous magnetization of the magnetic sublattice.

ments practically do not participate in the magnetism of these substances.* Investigations of magnetic scattering of neutrons have shown[62] that in the cases of both ferro- and antiferromagnetic d-metals there is a spatially ordered distribution of the spin magnetic moments. The usual theory of collectivized electrons gives a simple qualitative explanation of the fractional nature of the average atomic moments (cf., for example, [6] and also the survey [50]). The exchange interaction shifts the electronic energy levels for states with plus and minus spins relative to one another (just as the external field in paramagnetic materials, cf. Fig. 5), and this leads to the appearance of a resultant non-zero magnetization. Of course, the average atomic magnetic moment as a rule must also differ from the value of the moment for the isolated atoms or ions, for the case of non-metallic compounds. The reason for the absence of a contribution of the orbital magnetism in d-metals is still not completely understood. From the point of view of the model of collectivized electrons (within the framework of the simplest picture of a gas of Fermi particles), the whole contribution of the orbital states to the magnetism reduces to the Landau diamagnetism. In precisely this same way the band model of collectivized electrons cannot give a simple explanation of antiferromagnetism in the d-metals (concerning this question, cf. [63] and also the survey [50]). The explanation of antiferromagnetism (as well as the results of neutron diffraction studies for d-metals) requires an improvement of the band model and primarily the inclusion of the spatial inhomogeneities in the distribution of the electron density of the d-electrons in the crystal. This inhomogeneity is already imposed in principle in the very form of the wave function for an electron in a crystal [cf. formula (1.2) above]. Obviously for d-electrons, which are subjected to smaller collective effects than the outer valence s-electrons, the modulating factor in (1.2), $u_n(k, r)$ will play a greater role than the plane-wave factor $e^{ik \cdot r}$, the spatial distribution of electron density in the crystal will approximate more closely the localized distribution of the electrons in isolated atoms and ions as well as in ionic or valence compounds. In this connection a very important part is played by theoretical and, especially, experimental studies of form factors for the scattering of x-rays and neutrons in d-metals (cf., for example, [64] where a detailed bibliography of such studies is given, and the survey [50]), which would give exhaustive information concerning the actual shape of the electron density in crystals of the transition metals. However, this question is still by no means cleared up.† The problem of the electron

*The experimental proof of the spin nature of the magnetism in metals is a familiar result of gyromagnetic experiments (cf., for example,[8]).

†Here we need only recall, for example, the very recent discussion in connection with the work of Weiss and deMarco[65] on the measurement of x-ray form factors in d-metals of the iron group.

density in crystals is closely related to the question of calculating the exchange interaction parameter (exchange integral) for d-metals. Here there are still only two very crude approximations: calculation by the elementary band model[6] and on the model of localized electrons, which began from the work of Heisenberg[5] (cf., for example,[66] and also the survey [50]). Of course, these approximations cannot at all be regarded as satisfactory from a quantitative point of view. On the other hand, without a solution of this problem, the problem of the criterion for a state with atomic magnetic order in d-metals will remain unsolved, i.e., we will not be able to understand why we so rarely find such states in these metals.

Also important is the question of the participation of the valence s-electrons in the magnetism of the d-metals. Here two types of participation of these electrons in magnetically ordered states are possible. First, because of their exchange interaction with the d-electrons which have a spontaneous moment (so-called s—d-exchange),[67] these electrons will be polarized and will therefore make a contribution to the total moment of the crystal. This, so to speak, is the passive role of the s-electrons in the ferromagnetism of the d-metals. But in addition one may also imagine a more active role, namely, their participation in indirect exchange interaction between d- and d-electrons.[68] This last effect is especially important in the case of ferromagnetism of highly dilute solutions of d-metals in "diamagnetic solvents" (for example, solutions of Mn in copper, silver, etc.[69]), where the ions of the d-metal are separated by distances of the order of tens of inter-atomic spacings and one cannot speak of a "direct" exchange. (For more details, cf., for example, the survey[50]). The same effect of indirect exchange between conduction electrons apparently plays a predominant role in the establishment of ferromagnetism in the rare earth elements, to the treatment of whose magnetic properties we now turn.

B3. States of atomic magnetic order in the transition f-metals. Among the normal elements in the periodic table there are altogether 18 f-metals, and of these 14 are rare earths (with an incomplete 4f-shell) and four are actinides (with an incomplete 4f-shell). Experiment shows that almost all of the rare-earth metals at low temperatures are either ferromagnetic or antiferromagnetic, or may be in both ferro- and antiferromagnetic states (of course, in different temperature ranges). In contrast to the d-metals, the f-shell because of its small radius practically suffers no effect of crystalline collectivization, so that they therefore behave in a crystal as localized formations. Here one should only, of course, note that these electron shells are in a very definite surrounding and that that the fields of neighboring atoms act on them. These crystalline fields have a definite symmetry, so that their action can lead to a lifting of degeneracy of the

"free" ionic states which, in turn, may lead to a change in the magnetic properties (for more details, cf., for example, the monograph of Van Vleck[70] or the survey [50]). Studies of magnetic properties of rare earth metals are only just beginning. The reason for this is that up to now it has not been possible to obtain these metals in sufficient quantities and in a reasonably pure state. However, their investigation should disclose many interesting features because of their specific electronic structure. Most interesting in the case of these metals is the indirect character of the exchange interaction between f-shells with active participation of the 6s-conduction electrons.*

## 3. ELECTRICAL CONDUCTIVITY OF METALS

The conduction electrons in metals experience an accelerating effect from an external electric field $E_{ext}$. The finite value of the electrical resistance, as already pointed out in Sec. 1, is determined by the effects of inelastic scattering of electrons in the crystal, in which the electrons transmit the energy accumulated in the accelerating field to the lattice (Joule-Lenz heat). Within the framework of the classical electron theory of metals of Drude and Lorentz,[1] and also in the papers of J. I. Frenkel[2] there was already obtained the familiar formula for the specific conductivity $\sigma$ in terms of atomic constants:

$$\sigma = \frac{ne^2\tau}{m^*},\qquad(3.1)$$

where n is the density of conduction electrons, $m^*$ is their effective mass, e their charge, and $\tau$ the relaxation time (mean free time between collisions). The first three quantities characterize the mechanical parameters of the current carriers, determined from the dispersion law and the internal structure of the particle, and the last, the relaxation time, is a purely kinetic quantity determined by the character of the non-equilibrium statistical processes which are at the basis of the phenomenon of electrical conductivity of metals. Thus, the problem of the theory of electrical conductivity of metals consists on the one hand in obtaining a sufficiently accurate mechanical description of the current carriers in metals (i.e., the determination of their energy spectrum, or the equilibrium density matrix, etc.), and secondly in a correct formulation and a sufficiently precise solution of the purely statistical (kinetic) problem of the behavior of the system of current carriers when subjected to the action of an external electric field, and the interaction within the system itself of the current carriers, as well as their interaction with other particles forming the crystal (ion cores, various inclusions, etc.).

The computation of the electrical conductivity (3.1), as well as other kinetic coefficients (heat conductivity, Hall effect, etc.) starting with the work of Lorentz,[1] has usually been carried out using the Boltzmann[14] kinetic equation, where the distribution function f(k) of the current carriers is determined for non-equilibrium processes under the simultaneous action of the external accelerating field and the "damping" processes of collision. For a stationary, non-equilibrium process this equation has the following form:

$$\left(\frac{\partial f}{\partial t}\right)_f + \left(\frac{\partial f}{\partial t}\right)_{coll} = 0;\qquad(3.2)$$

The first term on the left side of equation (3.2) (the "drift" term) determines the change in the (equilibrium) distribution function under the action of an external electric field, while the second term describes the effects of "collision" of the current carriers in the metal which are being accelerated by the field. To solve (3.2), i.e., to find the non-equilibrium distribution function and then to calculate the value of the electrical current from the familiar Lorentz formula:[1] $j = e\overline{nv}$ (where the bar denotes an average statistical value of the product nv), one must find the specific form of the quantities $(\partial f/\partial t)_f$ and $(\partial f/\partial t)_{coll}$. In the derivation of the kinetic equation, one makes various approximations which require justification in each specific case (cf. for more detail, for example, Secs. 3 and 8 of Chapter 6 and Secs. 3 and 4 of Chapter 7 in the monograph [14], as well as the surveys [97,98]).

The starting point for the "derivation" of the kinetic equation is the general statistical equation for the density matrix (which is the analog of the Liouville equation of classical statistical mechanics; cf., for example, Sec. 6 in the monograph[37]):

$$i\hbar\dot{\hat{u}} = \hat{\mathscr{H}}\hat{u} - \hat{u}\hat{\mathscr{H}},\qquad(3.3)$$

where $\hat{u}$ is the density matrix (operator) of a quantized system, and $\hat{\mathscr{H}}$ is its Hamiltonian.* If we separate out in the Hamiltonian the term depending on the external electric field, which has the form $-e(E_{ext} \cdot \sum_j r_j)$, where $r_j$ are the coordinates of the particles in the system $(j = 1, 2, \ldots N)$, equation (3.3) takes the form

$$i\hbar\dot{\hat{u}} = \hat{\mathscr{H}}'\hat{u} - \hat{u}\hat{\mathscr{H}}' + eE_{ext}\left[\left(\sum_j r_j\right)\hat{u} - \hat{u}\left(\sum_j r_j\right)\right].\qquad(3.4)$$

Here $\hat{\mathscr{H}}'$ is the Hamiltonian excluding the terms containing the external field, and this in turn splits into an additive part $\sum_j \hat{\mathscr{H}}_0(r_j)$ and an interaction $\hat{V}$

$$= \sum_{j\neq j'} (r_j - r_{j'})$$ between the particles. Furthermore, if we go over from the density matrix for the total system (which depends on the coordinates of all the particles) to the reduced density matrices $\rho(r)$ depend-

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*One should also consider the possibility of the appearance of an indirect exchange between the electrons of the 4f-shell and the active participation not only of the 6s-conduction electrons, but also of electrons of the inner spin-saturated 5s- and 5p-shells.[71] Concerning the rare earth metals, cf. the surveys[19, 50, 72].

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*The problem of the derivation of the kinetic equation in quantum mechanics is treated, for example, in a paper of the author.[73] These questions are also considered in the monographs[74-76].

ing on one coordinate, and $\sigma(\mathbf{r}, \mathbf{r}')$ depending on the coordinates of two particles, Eq. (3.3) finally takes the form

$$i\hbar\dot{\varrho} = \hat{\mathcal{H}}_0\hat{\varrho} - \varrho\hat{\mathcal{H}}_0 + \mathrm{Sp}_r(\hat{V}\hat{\sigma} - \hat{\sigma}\hat{V}) + e\mathbf{E}_{ext}(\mathbf{r}\hat{\varrho} - \hat{\varrho}\mathbf{r}), \quad (3.5)$$

where $\mathrm{Sp}_r$ is the trace (spur) of the operator $(\hat{V}\hat{\sigma} - \hat{\sigma}\hat{V})$, taken without summing over one of the coordinates, namely $\mathbf{r}$. The appearance in (3.5) of the "binary" density matrix $\sigma(\mathbf{r}, \mathbf{r}')$ expresses the specific features of the system of interacting particles. As pointed out in the preceding footnote, in [73] those approximations were indicated which are usually used in order to obtain the kinetic equation of the Boltzmann type from the "exact" equation (3.5). The most important assumption in this paper is the condition that the time $\tau$ between collisions [which enters, for example, in formula (3.1)] should considerably exceed the duration of the collision $\Delta t$. As Peierls and Landau showed (cf. [14]), for example, for the "collisions" of conduction electrons with the thermal vibrations of a crystal lattice, the duration of the collisions is $\Delta t = \hbar/kT$. Only when $\tau \gg \Delta t$ are the assumptions valid which are the basis of the derivations [14,73] of the kinetic equation from (3.3).

In recent years, beginning with the well-known papers of Bogolyubov, [74] there has begun the systematic theoretical investigation of improved methods for calculating kinetic coefficients in solids, including the electrical conductivity of metals. Let us discuss briefly some of these methods.

First of all, we should recall papers in which attempts have been made to improve the solution of the usual kinetic equations which are used in the band theory of metals and which were first introduced in the papers of Bloch [15] and Peierls. [14,16] However, these papers can hardly be regarded as very fruitful, since they do not eliminate the initial crude assumptions which are at the basis of the whole method of the Boltzmann kinetic equation as used in the elementary band theory of metals.

A presentation of this direction of work can be found by the reader in the paper of MacDonald, White, and Woods, [77] where they give a bibliography of appropriate papers and a comparison of the theoretical computations with experimental data for the electrical conductivity of alkali metals.

Physically much more interesting and consistent is the direction which involves an improvement in the initial kinetic equation itself. Here we should mention first of all the previously cited work of Bogolyubov [74] as well as the work of Klimontovich and Temko, [78] Silin, [79] Eleonskiĭ, Zyryanov, and Silin. [80] The important feature of these papers is the more correct inclusion of the binary distribution function and also the more accurate computation of collision integrals without the assumption that the external field is small. Unquestionably, this method for improving the kinetic treatment of statistical phenomena in crystals is very promising.

A very important direction in statistical mechanics of irreversible processes was started in the papers of Kubo and Tomita [81] and Kubo. [82] In these papers there was proposed a method in which formally no kinetic equation is introduced, but one carries out a determination of the non-equilibrium kinetic coefficients directly by means of the density matrix which describes the non-equilibrium system of interacting particles. (In the case of the electrical conductivity of metals this is the electron-phonon system.) The advantage of the Kubo-Tomita method is that it permits one simply to find a generalized Gibbs distribution for a non-equilibrium system, and then to use all the advantageous features of the universal Gibbs method for the case of irreversible processes. Kubo's method was used for the particular case of electrical conductivity in papers by Nakano, [83] Klinger, [84] Van Hove and Verboven. [85]

Another variant of the theory of non-equilibrium processes in solids was developed in papers of Van Hove [86] and Kohn and Luttinger. [87] In this method also one avoids the use of a kinetic equation of the Boltzmann type. An attempt is made to solve the equation of type (3.4) for the density matrix by using perturbation theory (in the approximation linear in the field), in which one includes damping. This method enables one to obtain a more general transport equation which takes into account some of the non-diagonal elements of the density matrix (which are dropped in obtaining the usual kinetic equation, cf. [73]). This approach is especially attractive in those cases where one must include higher terms in the interaction of the current carriers with the scatterers in the perturbation theory series (for example, in the case of a computation of the anomalous Hall effect in ferromagnets [88]).

We also mention that, essentially, Kubo's method is equivalent to the method of temperature Green's functions (concerning this question, cf. Sec. 4 in the survey [43]). In a paper of Konstantinov and Perel' [89], within the framework of the method of temperature Green's functions, [45] they have also used the diagram technique of quantum electrodynamics [18] for the computation of kinetic coefficients.

This briefly is the situation from the methodological standpoint. Now let us also enumerate very briefly the main results obtained in the theory of electrical conductivity of metals.

For the case of normal (non-transition) metals, within the framework of band theory two specific very important questions were already solved concerning the temperature behavior of the phonon part of the electrical resistance of these metals. For the high temperature region $T > \theta_D$, where $\theta$ is the Debye temperature of the metal, there was obtained a linear law $\rho = \alpha T$. This result was already obtained by J. I. Frenkel [4] from elementary arguments concerning the fact that the cross section for scattering of electrons by lattice vibrations is proportional to the square

of the amplitude of the vibrations, which in turn is proportional to the mean energy $\sim kT$. From this one finds for the scattering probability $1/\tau \sim T$, and by virtue of (3.1) we obtain a linear increase with temperature for the specific electrical resistance $\rho \sim \alpha T$. In the low temperature region ($T \ll \theta_D$), a different result is obtained, which is found in the papers of Bloch[15] and Peierls,[14,16] and which is related to the quantum statistics of Fermi and Bose particles. On the other hand, the scattering cross section is proportional to the change in the number of phonons with temperature, which for $T \ll \theta_D$ is proportional to the cube of the temperature $\sim T^3$. Furthermore, the efficiency of each collision varies with the square of the temperature, so that the scattering cross section $1/\tau$ varies as $T^5$. From this it also follows that in the low temperature range the phonon part of the electrical resistance of non-transition metals varies according to a $T^5$ law. Both these conclusions are general in character and are not associated with any crude model pictures. However, aside from the phonon part of the electrical resistance, in real metals there are also other mechanisms for scattering of the conduction electrons which make a contribution to the electrical resistance. First of all, we should recall the mechanism of scattering by non-thermal lattice defects (foreign atoms, vacancies at lattice sites, dislocations, etc.). In such a mechanism there is always a considerable non-thermal part which makes a fundamental contribution to the so-called residual electrical resistance of metals, which is obtained by extrapolating the $\rho(T)$ curve to $T = 0°K$. Also of great interest is the temperature-dependent part of the electrical resistance, which is caused by the scattering mechanism described above (on lattice defects). This temperature dependence can be determined first of all by the interference between the phonon and impurity mechanisms of scattering[90] and also by the fact that the value, the potential, and the nature of the distribution of defects in the crystal lattice may vary with the temperature.[91]

Another question that has been treated is the problem of the deviations from Ohm's law in metals in strong fields and at high current densities. For example, a paper of Shabanskiĭ is devoted to this problem.[92]*

*We are unable here even to enumerate all the results obtained in the theory of electrical conductivity of metals. Let us only recall some of them which are of general physical interest. First of all, as already mentioned in Sec. 2, in paragraph A3, from the Fermi character of the system of conduction electrons it follows that one can have oscillatory effects for the kinetic coefficients of metals, including their conductivity. This effect was observed experimentally by Shubnikov and de Haas;[102] the most complete theoretical explanation of this phenomenon is found in the framework of the method of I. M. Lifshitz.[103] Special attention is devoted to the dependence of the electrical conductivity of metals on the frequency of an external variable electromagnetic field. Particular interest has been devoted to the study of the phenomenon of anomalous skin effect in metals,[104] which occurs when

It is known from experiment that the electrical conductivity of liquid metals differs little from the electrical conductivity of solid crystalline metals. The only thing that happens is that there is a jump in the electrical conductivity at the melting point, which is connected with the jump in the specific volume of the metal at this transition point. Landau and Kompaneets[93] pointed out the need in the case of liquid metals to distinguish between the electrical resistance at constant volume and at constant pressure. The first quantum mechanical calculation of electrical resistance for liquid metals was carried out in a paper by Shubin.[94] In this paper it was shown that a conduction electron in the non-periodic and almost uniform potential will behave like an electron in a weakly periodic potential ("almost free electron" in the band theory[14]). It was also shown in this paper that if the thermal motion in a liquid metal can be treated as a small oscillation around the position of stable equilibrium, then (despite the random distribution of the centers of oscillation) the specific resistance should vary with temperature according to a linear law, $\rho \sim T$. In addition, there was also pointed out a mechanism for scattering of electrons on ions in the lattice by direct scattering, which explains the residual resistance of liquid metals. The temperature dependence of this contribution to the electrical resistance also is linear, $\rho \sim T$. The theory of electrical resistance of liquid metals was further developed in a paper of Zyryanov,[95] who, using the plasma model of a metal and the calculations of the phonon part of the electrical resistance (see paper[34]) took account of scattering of the conduction electrons on the "small-scale" (relaxational) fluctuations of the ionic lattice and obtained a quantitative explanation of the temperature dependence of the electrical resistance of liquid metals and its jump at the melting point.

Investigations have also been made of the electrical resistance of metallic, disordered, and ordering alloys. We do not have the space here to discuss this interesting question and refer the reader to the general monograph on this problem recently written by A. A. Smirnov.[96]

The transition metals also have fundamental peculiarities with respect to electrical resistance. These peculiarities are related first of all to the complex character of the electronic system of these metals (the system of conduction electrons includes, in addition to the former valence electrons, electrons from

the mean free path (at sufficiently low temperatures and high frequencies) becomes comparable to or greater than the depth of the skin layer. In this connection great interest has been shown in studies of electrical conductivity taking account of the space-time dispersion in a metal.[105] The effect of electron-electron collisions on the electrical resistance of metals has also been considered. The calculations which have been made show that the additional term in the electrical resistance caused by such collisions has a temperature dependence of the form $T^2$ (cf., for example, Sec. 5 in Chapter 6 of the monograph[14]).

the unfilled d-shells), and secondly with the additional possibility of scattering on inner (d- and f-) shells and on their spin states. A more detailed survey of this problem can be found in the paper of the author and Izyumov.[50]

In conclusion, we may state that the theory of the electrical conduction and the magnetic properties of metals, as well as their experimental investigation, has received extremely broad development since the work of J. I. Frenkel, who laid the foundation for this branch of the present-day physics of solids.

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