

State of the conduction electrons and the work function of a metal

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Abstract. The condition for a minimum of the bulk energy of a metal is used to determine the chemical potential of the conduction electrons. This potential is measured from the value of the energy far from the metal and is equal (with the opposite sign) to its work function. Suggestions are made as to the reasons why a very simplistic description of the problem leads to results that do not conflict with the experimental data.

The unusually long 'lifetime' of the books by Yakov Il'ich Frenkel' is due to this author's ability to explain the nature of complex quantum effects in a simple and clear manner. This applies particularly to the physics of the condensed state. Frenkel' justly said that the more complex the effect, the simpler should be the theory. His *Vvedenie v Teoriyu Metallov* (Introduction to the Theory of Metals) [1] has gone through four editions and, although the last one was published in 1972, it is still a book used actively by physicists and physical chemists working at different levels. A comparison of the content of this book with those published recently (for example, A A Abrikosov's *Fundamentals of the Theory of Metals* [2]) shows that Yakov Il'ich treated the theory of metals much more comprehensively than the modern authors. His *Introduction to the Theory of Metals* contains chapters dealing with the theory of melting, ordering alloys, kinetics of precipitation of solid solutions, and strength and plasticity of metals. Three (out of 22) chapters of the *Introduction* deal with the electron (band) theory of metals.

The rapid development of the electron band theory of metals has, on the one hand, led to the understanding and sometimes the discovery of fine quantum-mechanical properties of metals (galvanomagnetic phenomena, cyclotron resonance, Shubnikov–de Haas and de Haas–van Alphen effects, various acoustoelectronic effects, etc.) by relating them to the electron energy spectra ('fermiology') and, on the other, has provided a first-principles explanation of superconductivity as a phenomenon due to the formation of Cooper pairs of electrons by their interaction involving

the virtual-phonon exchange (see, for example, Refs [3] and [2]).

In the band theory all the attention is on the electron system of a metal, i.e. on the conduction electrons moving in the field of the crystal-lattice ions; the interaction of electrons with one another is allowed for by the Landau theory of a Fermi liquid [4]. The expressions derived on the basis of the Fermi-liquid theory have made it possible to avoid the tiresome complexity of the discussion based on the direct allowance for the electron–electron interaction.

In the band theory the ion lattice of a metal is the space where the conduction electrons 'live' (\mathbf{r} space). This space is periodic so that the state of an electron (or any other quasiparticle) can be described by introducing the quasimomentum vector \mathbf{p} , very similar to the momentum vector, but differing from the latter because it is specified within one reciprocal-lattice cell: the \mathbf{p} space is periodic.

Introduction of the periodic \mathbf{r} space and the associated periodic \mathbf{p} space 'liberates' the metal electrons from the influence of the external world surrounding a sample. The boundaries of a sample (if its finite dimensions have to be allowed for) provide an additional channel for the scattering of the conduction electrons and/or a region where specific two-dimensional quasiparticles can congregate (these particles include the quanta of surface and Rayleigh acoustic vibrations, Tamm levels, surface polaritons, etc.). The feasibility of crossing the boundary of a sample, i.e. the escape of an electron outside the sample, is usually ignored completely in the band theory.

However, there are phenomena which cannot be described if the escape of an electron from a metal is ignored. This applies particularly to the various types of emission (thermionic emission, cold emission, external photoelectric effect, ion–electron emission). They also include the contact potential, operation of galvanic cells, etc. In all those phenomena in which the escape of an electron from a metal into the surrounding space or the transition of an electron from one sample to another has to be allowed, the characteristic known as the *work function* assumes a decisive importance. The work function W is the minimum "work that has to be done on a particle if its removal occurs in a thermodynamically reversible manner" [5]. This function is always positive ($W > 0$) since a point charge is attracted to a neutral body (in particular, to a conductor). Introducing $W = e\phi$, where e is the charge of a particle, we can demonstrate that the sign of the work-function potential ϕ is identical with the sign of the charge (for electrons we have $e < 0$).

It is evident that the positive nature of the work function of an electron is due to the fact that the electrons in a metal are in a potential well created by positively charged ions.

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Received 28 December 1993

Uspekhi Fizicheskikh Nauk 164 (4) 375–378 (1994)

Translated by A Tybulewicz

Since the conduction electrons are degenerate (the temperature T is usually much less than the degeneracy temperature $T_F \sim 10^4 - 10^5$ K), the escape occurs from the Fermi level and the following problem (which is outside the framework of the band theory of metals) has to be faced: what is the position of the Fermi level relative to the external world?

The problem is complicated by the dependence of the work function of an electron not only on the nature of the conductor, but also on its surface (for example, on the direction of the surface relative to the crystallographic axes if the conductor is a single crystal, on the degree of surface con-tamination, on the presence of an oxide film, etc.). At first sight this might seem to be strange because it is assumed intuitively that the removal presumes the transfer of electrons to 'infinity', i.e. to a point very far from the surface of a metal where no forces related to the charge of a semiconductor can act (we are assuming that the energy of a charge at rest at infinity—far from the surface of a metal—is zero). In fact, the work function represents the transfer of a charge from a conductor to its surface, where the potential depends on the surface structure. The reference data on the work function of different faces of single-crystal conductors with clean surfaces do not differ very greatly from one another. For example, the work function for different faces of a tungsten single crystal is as follows: 5.3 eV, 4.4 eV, and 4.6 eV for the (110), (111), and (100) faces, respectively [6]. We can ignore this difference if we confine ourselves to just a rough qualitative estimate of the work function (see below).

In a macroscopic (average) description a metal it should be regarded as locally neutral, since the Debye–HuSckel radius of the conduction electrons is of the order of (or even less than) the lattice constant a (see Chapter 17 in Ref. [7]). In other words, the average charge density in a metal is $\rho(r) \equiv 0$. Consequently, the potential well for the conduction electrons is in fact created by the potential of a double layer, which is located in a thin surface region where $\rho(x) \neq 0$ (x is the coordinate along the normal to the surface). The jump of the potential at the metal–vacuum interface is (see, for example, [5])

$$\delta W = 4\pi \int_{-\infty}^{\infty} x\rho(x) dx . \quad (1)$$

Here '∞' means the distance which is large compared with the linear size a of a unit cell. We can 'acquire a feeling' how Eqn (1) operates by considering the simplest model in which the charge density differs from zero in the interval $[-d, d]$, $x = 0$ is the boundary of a crystal, and

$$\rho = \begin{cases} \rho_0 x d^{-1}, & |x| < d, \\ 0, & |x| \geq d. \end{cases} \quad (2)$$

It then follows from Eqns (1) and (2) that

$$\delta W = \frac{8\pi}{3} \rho_0 d^2 . \quad (3)$$

The characteristic value ρ_0 is naturally e/a^3 and we have $d \sim a$, since it cannot differ too much from the Debye–HuSckel radius. Therefore, the jump of the potential is $\delta W \sim e/a$, i.e. it is identical with the characteristic potential of an ion (it is assumed that the degree of ionisation is unity). This estimate shows above all that the exact work function cannot be calculated without knowledge of the specific structure of the crystal surface. Calculations should

be carried out in a self-consistent manner and we cannot ignore the position of the bottom of the conduction band or the Fermi energy, which are the bulk characteristics of the electron system in the ion lattice of a metal (see below and, for example, Ref. [8]).

However, the similarity of the work functions of different faces of the same crystal suggests that the structure of the unit cell near different faces is approximately the same and, moreover, that it differs little from their structure in the bulk. This is essentially the main model approximation adopted in the present paper. It follows from this approximation that the work function is equal to the Fermi energy measured from the zero level, which is the value of this energy far from a metal. This is manifested particularly clearly in the figure reproduced here (Fig. 1) from Ashcroft and Mermin's *Solid State Physics* [7] (Fig. 18.1b in that book). If the work function were to be measured for deliberately formed crystal faces with large Miller indices, along which the charge distribution differs considerably from the distribution along close-packed planes, the work functions might differ considerably from those usually given in reference books.

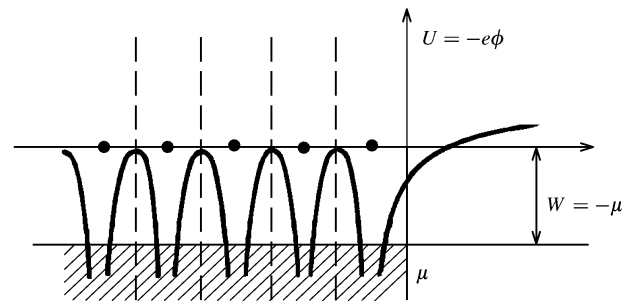


Figure 1. Crystal potential U (or the electrostatic potential $\phi = -U/e$) along a row of ions in a crystal. At a large distance from a crystal we have both U and ϕ tending to zero. The negative Fermi energy is marked on the vertical axis. The shaded region represents schematically the filled electron states. The removal of an electron from a metal is possible if it is given an energy $W = -\mu$ (see Fig. 18.1b in Ref. [7]).

In connection with the structure of a double layer on the surface of a metal and the role of this layer in the determination of the work function one must mention the pioneering work of Frenkel' on 'Electrical double layer on the surfaces of solids'. This work was carried out in December 1916 and published in two consecutive volumes of *Zhurnal Russkogo Fizikokhimicheskogo Obshchestva* [49 100 (1917); 50 5 (1918)]. This paper begins with the words "The existence of electrical double layers on metal surfaces has recently been finally established by a number of investigations of the emission of free electrons by metals under the influence of heating (thermionic or Richardson effect) or illumination (photoelectric effect)."

At temperatures $T \ll T_F$ the Fermi energy is very nearly equal to the chemical potential $\mu = \partial E / \partial N_e$, where E is the energy and N_e is the number of electrons in a conductor. An attempt to estimate the chemical potential of the conduction electrons is made in Ref. [9] subject to allowance for the position of the bottom of the potential well, i.e. by 'linking' this potential to zero energy outside the metal.

The calculations made by A A Abrikosov [10] show that the potential energy of a system of ions and electrons, consisting of the energy of the Coulomb interaction of electrons and ions and of the exchange energy of electrons, is

$$\bar{U} = -C(z)e^2 N z (nz)^{1/3} . \quad (4)$$

Here N , is the number of ions with a charge ze in a crystal; $n = N/V$ is the density of these ions; nz is the electron density; V is the volume of a crystal (the density is the number of particles per 1 cm^3); the factor in the above expression is $C(z) \sim 1$ and it depends on the lattice structure. In terms of the same notation the Fermi energy ε_F of the conduction electrons, measured from the bottom of the potential well, is

$$\varepsilon_F = (3\pi^2)^{2/3} \hbar^2 (2m)^{-1} (nz)^{2/3} , \quad (5)$$

and the total kinetic energy of electrons is

$$E_e = -\frac{3}{5} N z \varepsilon_F . \quad (6)$$

The use of Eqns (5) and (6), valid for a gas of free electrons, needs some comment (which is given below).

The total energy of electrons and ions is the sum of their potential and kinetic energies. According to Eqns (4)–(6), if ions are assumed to be immobile (i.e. if the temperature effects are ignored), the result is

$$E = \frac{3}{5} (3\pi^2)^{2/3} \frac{\hbar^2}{2m} N z (nz)^{2/3} - C(z)e^2 N z (nz)^{1/3} . \quad (7)$$

In the above expression the density of ions should be regarded as a parameter which has to be found by energy minimisation. This requires some explanation. We are assuming that the degree of ionisation z is characteristic of a metal atom (for example, the number z is equal to the valence of an atom) and that $n = N/V = 1/v_0$, where v_0 is the volume per one ion. Therefore, minimisation with respect to n means determination of the crystal structure, i.e. of the unit-cell volume for which the bulk energy is minimal. Equating $\partial E/\partial n$ to zero, we find that the expressions corresponding to the equilibrium density $n = n_0(z)$ are

$$E = -\frac{3}{5} N_e \varepsilon_F(n_0), \quad N_e = N z . \quad (8)$$

It should be noted that the result obtained is independent of the actual dependence of the factor C on the degree of ionisation z . The important points to note are that $\varepsilon_F \propto n^{2/3}$ and $\bar{U} \propto n^{1/3}$.

It follows directly from Eqn (8) that the chemical potential of the conduction electrons (for a fixed density of these electrons) is

$$\mu = -\frac{3}{5} \varepsilon_F(n_0) . \quad (9)$$

Consequently, we find that

$$W = \frac{3}{5} \varepsilon_F(n_0) . \quad (10)$$

†In the paper cited earlier [9], two of the present authors determined the equilibrium density of carriers and the total energy of the conduction electrons by the virial theorem. It was pointed out in Ref. [9] that the value of n_0 agrees with the real values of the electron density in metals.

The fact that the work function is governed solely by an electron characteristic is naturally a consequence of the simplifying assumptions made here and in Ref. (9).

The principal assumptions are as follows:

(1) A double (dipole) layer at the boundary of a sample is constructed so as to ensure the same jump in the potential for all the faces and the structure of the potential of both ions and electrons is not disturbed by the proximity of the boundaries of the sample (Fig. 1). A more rigorous formulation of the problem (even within the framework of the macroscopic description) requires, after calculation of the equilibrium density by minimisation of the bulk energy of Eqn (7) and introduction of certain assumptions on the surface structure, minimisation of the surface energy and calculation of the exact value of the jump of the potential and of the work function. The reasonable (qualitative) agreement between Eqn (10) and the experimental data allows us to restrict ourselves to the assumption formulated earlier (and repeated here).

(2) The electrons in a metal form a *free* electron gas with the quadratic isotropic dispersion law.

The second of these assumptions may seem rather strange. After all, it follows from it that the Fermi surface of a metal is a sphere, whereas—as pointed out above—one of the main achievements of the electron theory of metal is the explanation of the complex structure of the Fermi surfaces and of their role in accounting for the various properties of metals. However, although it may seem paradoxical, the two statements are not in conflict. Naturally, in discussing the dynamics of the conduction electrons (particularly in an external magnetic field) we must allow for the specific geometric structure of the Fermi surface, but in the calculation of the total energy of the conduction electrons the Fermi surface of many metals can be deduced from the Harrison model in which the principal assumption is that the complex structure of the Fermi surface (various sheets, pockets, etc.) is the result of degeneracy of the states corresponding to the boundaries of the Brillouin zone. In other words, the Fermi surface of many metals, which plays an important role in the dynamics of the conduction electrons, is the result of cutting up of the Fermi sphere of free electrons (see §11 in Ref. [3]; §§14 and 3 in [2]). This means that the total energy of the conduction electrons in a real metal should not differ greatly from the energy of a gas of free electrons with the same density. This is supported by Fig. 1 of Ref. [9] (see preceding paper). The experimental values of the work function W_{exp} are compared there with the theoretical value of Eqn (9), which should be compared with Eqn (31) of Ref. [9]:

$$W_{(\text{eV})} \cong 15.6 \left(\frac{\rho_M z}{A} \right)^{2/3} . \quad (11)$$

Here, A is the mass number of the element and ρ_m is the mass density (g cm^{-3}). For some metals (Ca, Sr, Cu, and Hg) the experimental values of the work function agree almost exactly with the results of calculations carried out on the basis of Eqn (11). In the case of other metals the agreement is poorer, and the ratio W/W_{exp} lies within the limits 0.5–1.75, which in our opinion is quite satisfactory in view of the rough approximation which has been used.

We shall not deal with all the refinements that should have been considered in a rigorous quantitative theory, but point out the need to allow for the Fermi-liquid effects,

renormalisation due to the interaction of electrons with phonons, etc. Naturally, in the development of a rigorous theory these effects cannot be ignored, but there are no grounds for assuming that the results would change by an order of magnitude. There is a group of metals (K, Na, Rb, Cs) whose Fermi surfaces are spherical. The degeneracy at the Brillouin zone boundaries, mentioned above, is not important in the case of these metals and the whole of the difference between the conduction electrons and free electrons in these metals is manifested by the difference between their effective mass and that of a free electron. However, this difference is only 10%–20%! Our calculations cannot pretend to be within these error limits.

Our analysis suggests a comment about the lack of success in detection of oscillations of the work function in a quantising magnetic field [11] in the case of three-dimensional samples, although an estimate of $\delta\mu/\mu$ made many years ago [12] would seem to allow observation of the oscillations† ($\delta\mu$ is the correction, oscillating with the magnetic H , to the chemical potential μ of the conduction electrons). Only the change in the dynamics of the conduction electrons in a magnetic field H is allowed for in the paper by Kaganov et al. [12]. The role of the conduction electrons in creation of the potential well is not considered. If our estimate of the work function is correct, it is obvious that a change in the dynamics of electrons in fields $H \neq 0$ should alter the electron energy of Eqn (6) [and possibly also the potential energy of the interaction of electrons and ions of Eqn (4)]. According to the theory of the de Haas–van Alphen effect (§§15–17 in Ref. [3]), the maximum relative amplitude of the energy oscillations is

$$\frac{\delta E}{E} \propto \left(\frac{\beta H}{\varepsilon_F} \right)^{5/2}, \quad \beta = \frac{e\hbar}{m^*c},$$

whereas

$$\frac{\delta\mu}{\mu} \propto \left(\frac{\beta H}{\varepsilon_F} \right)^{1/2}.$$

Since $\beta H \ll \varepsilon_F$ (this is one of the conditions for the appearance of oscillations), the difference between the power exponents (5/2 instead of 1/2!) may possibly account for the absence of oscillations of the work function.

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It seems appropriate to publish this paper in the issue of *Uspekhi Fizicheskikh Nauk* celebrating the centenary of the birth of Yakov Il'ich Frenkel'. The amazing intuition, which enabled Yakov Il'ich Frenkel' to simplify the discussion right to the limit without losing the qualitative features of the effect, cannot be learned. However, attempts to achieve this are permissible. We would like to believe that we have not crossed the limit and have captured specifically the qualitative side of the topic: electrons and ions, creating together the potential well for electrons, are

so strongly coupled that the height of the barrier which an electron has to overcome when leaving a metal can be at least approximately described only in electron terms. Specific results [Eqns (10) and (11)] may and should naturally be refined, but—in our opinion—the calculation of the work function (and, naturally, of various emission properties) is impossible without direct allowance for the interaction of electrons with the ion framework, which makes it possible to find the position of the conduction bands relative to zero, which is the energy outside a metal far from its boundaries.

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†It is stated in Ref. [13] that there should be no oscillations of the work function because of the inhomogeneity of the state of electrons near the boundary of a sample in fields $H \neq 0$.