Static skin effect on atomically pure tungsten and molybdenum surfaces

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The static skin effect in thin tungsten and molybdenum samples is investigated. The measurements are performed on plane-parallel plates with atomically pure surface or else surfaces oxidized in air or coated by a monatomic film of absorbed matter. It is shown that cleaning of the surface increases the coefficient p of specular reflection of the electrons from the boundary and modifies the surface conductivity σ_{sur}. Cases when the magnetic field is oriented in the plane of the plate or perpendicular to it are studied in detail. In the first case σ_{sur} increases with increasing p and in the second it decreases. These regularities are governed by the peculiarities of the electron trajectories in the magnetic field. The value of p for an atomically pure surface is found to be 0.8 for W and 0.2–0.6 for Mo. The measurements are performed at a temperature 4.2 °K in air and in high vacuum (10^{-11} mm Hg). The variation in crystal resistance due to surface cleaning ranges from tens to hundreds per cent.

It is known that the resistivity of metals having equal electron and hole densities increases quadratically in a strong magnetic field. A characteristic parameter determining this dependence is the ratio $\gamma = r/l$, where r is the Larmor radius and l is the carrier mean free path. In pure perfect crystals at low temperatures, when l reaches several millimeters, the resistivity, which depends on the magnetic field like $\rho = \rho_0/\gamma^2$, increases by a factor 10^4—10^5. At the same time, the condition $l \sim d$, where d is the thickness of the conductor, is easily satisfied in thin crystals. In this case, the scattering by the boundary is significant and can determine the average kinetic characteristics of the crystals.

In the presence of a magnetic field, the interaction of the electrons with the boundary leads to a redistribution of the current over the conductor cross section and of the current density at the surface, where the mobility of the electrons is much larger in some cases than in the volume. This phenomenon was named the static skin effect[1].

In a plane-parallel plate, the surface current connected with the scattering of electrons by the boundary depends on the orientation of the sample in the magnetic and on the character of the interaction with the surface.

Cases when the magnetic field is oriented in the plane of the plates or is perpendicular to it differ in principle (we always have here $\mathbf{H} \perp \mathbf{j}$, where $\mathbf{j}$ is the direction of the current). The distinct behavior of the electron trajectories in the magnetic field is the reason why in a parallel field the surface current is proportional to the coefficient of specularity of carrier reflection from the boundary, while in a perpendicular field it is inversely proportional to it. Rotation of the plate in a magnetic field through 90° should lead for this reason to a change in the sign of the size effect: an increase in the diffuseness, e.g., should cause an increase of the resistance in a parallel field and a decrease of the resistance in a perpendicular one.

These relations can be observed experimentally, since the specularity coefficient is not a characteristic of the crystal and is determined by the state of the surface. In oriented single-crystal surfaces, it is possible in principle to realize total specular reflection[2,3]. To this end it is necessary that the surface atoms preserve the translational symmetry of the crystal lattice of the volume.

Naturally, real surfaces have machanical imperfections, or else are coated with a film of adsorbed matter or with an oxide layer. These formations destroy the periodic character of the microrelief of the surface and make specular reflection impossible. The diffuseness is preserved also in the case when foreign atoms combine into two-dimensional ordered structures, whose lattice periods differ from the lattice period of the host metal.

Purification of the crystal in high vacuum bares the true metallic surface and greatly increases the specularity of the electron reflection. Subsequent deposition of controllable amounts of impurity make it possible to regulate the specularity coefficient in a wide range. The thus attainable changes of the magnetoresistance of thin crystals make amount to tens and hundreds per cent.

The present paper is devoted to an experimental investigation of these irregularities in perpendicular and parallel magnetic fields in thin tungsten and molybdenum plates (these metals have equal electron and hole densities, $N_1 = N_2$). The first results of this research for tungsten was published earlier[4,5].

SAMPLES AND EXPERIMENTAL PROCEDURE

In general outline, the experimental procedure does not differ from that described in[5]. The measurements were performed on samples oxidized in air and under conditions of high vacuum (10^{-11} mm Hg) in sealed glass devices at liquid helium temperature. The samples were rectangular plates measuring 8 × 2 mm and were cut from single-crystal blanks of high purity with ratio $\rho(300°K)/\rho(4.2°K) = 33 \times 10^3$ for tungsten and 4×10^3 and 20×10^3 for molybdenum. The plate surfaces were polished and bright-dipped. The samples were oriented within ±0.3° in the plane of the (110) face with an x-ray goniometer. The electric current flowed in the ⟨100⟩ direction. At this orientation, the directions $\mathbf{H} \perp \mathbf{n}$ and $\mathbf{H} \parallel \mathbf{n}$ were physically equivalent (here n is the normal to the surface of the plate).

The construction of the vacuum instrument, the method of securing the samples in it, and the procedures

connected with further processing of the crystals in vacuum at high temperature are described in detail in[5]. We note here only that the final purification of the crystals in vacuum immediately prior to the experiment was already carried out in the cryostat with the helium poured-in. The samples were heated to 2500°K by the Joule heat (the current needed for this purpose was 45–50 A) or by electron bombardment. This procedure prevented a residual-gas film from becoming adsorbed on the crystal. The purity of the initial surfaces, was monitored by measuring the work function.

Foreign matter was evaporatored on the surface from sources placed in the "warm" part of the experimental vacuum device. The adsorbates were oxygen or silver. Just as in[5], the oxygen was evaporated from a heated platinum tube filled with copper oxide. The source of the silver atoms was a cylinder of 6 mm diameter. The body of the evaporator was made of molybdenum plate; it had a hole of 1.5 mm diameter for the passage of the evaporated matter and was surrounded by a ring cathode. The silver was heated to the evaporation temperature by electron bombardment of the evaporator body. The sources were carefully conditioned during the evaporation process. The silver was evaporated on a cooled crystal. The angular dependences of the magnetoresistance were measured on samples oxidized in air in an electromagnet at a field intensity 8 kOe. The measurements in vacuum were carried out in fields up to 10 kOe in an electromagnet (for the $\mathbf{H} \perp \mathbf{n}$) orientation or in a solenoid (for the $\mathbf{H} \parallel \mathbf{n}$ orientation).

EXPERIMENTAL RESULTS

Figures 1–3 show the results of the measurements of the angular dependences for three series of tungsten and molybdenum samples. The plate thickness decreased in succession from ~1 to 0.05–0.04 mm. The results show quite definitely the existence of a size effect, which is observed already in relatively thick crystals at all orientations of the magnetic field.

In a parallel field the effect is most noticeable (this orientation corresponds to the angle zero in the figure). In "dirty" molybdenum crystals, for which $\rho(300°K)/\rho(4.2°K) = 4 \times 10^3$, the size effect appears at

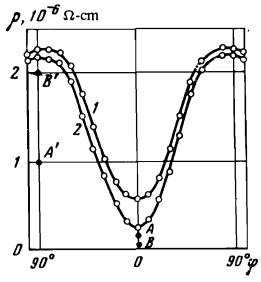

FIG. 1

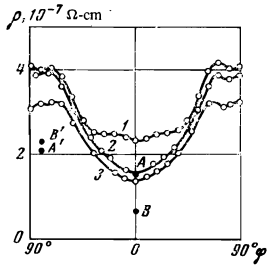

FIG. 2

FIG. 1. Angular dependences of the magnetoresistance $\rho(\varphi)$ for tungsten samples with $\rho(300°K)/\rho(4.2°K) = 33 \times 10^3$ at H = 8 kOe. 1–d = 0.63 mm, 2–0.39 mm. The points A and A′ denote the magnetoresistance of a thin plate with d = 0.06 mm prior to the cleaning of the surface in vacuum, while B and B′ denote the magnetoresistance after cleaning

FIG. 2. Angular dependences of the magnetoresistance $\rho(\varphi)$ for molybdenum samples with $\rho(300°K)/\rho(4.2°K = 20 \times 10^3$ at H = 8 kOe. 1–d = 0.62 mm, 2–0.40 mm, 3–0.27 mm. Points A and A′ denote the magnetoresistance of a thin plate, d = 0.15 mm, prior to the cleaning of its surface in vacuum, while B and B′ denote the magnetoresistance after cleaning.

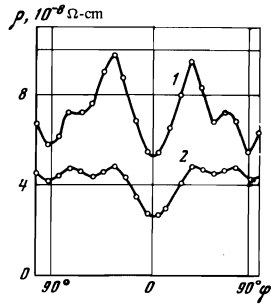

FIG. 3. Angular dependences of the magnetoresistances $\rho(\varphi)$ for molybdenum samples with $\rho(300°K)/\rho(4.2°K) = 4 \times 10^3$ at H = 8 kOe. Curves 1–for d = 0.72 mm; 2–for 0.04 mm. In the measurements, the electric current was made to flow in the ⟨110⟩ direction.

smaller thicknesses (Fig. 3). The thinnest crystals were purified in vacuum. The surface treatment of the plates has led to significant changes in their resistance, namely, it decreased in a parallel magnetic field and increased in a perpendicular field. The results of these observations are shown in Figs. 1 and 2. Point A in Fig. 1 corresponds to the magnetoresistance of a tungsten plate (d = 0.06 mm) with a real surface. It was measured in a parallel magnetic field on a sample oxidized in air. Cleaning the crystal in vacuum led to an almost sixfold decrease of its magnetoresistance (this final resistance is designated B in Fig. 1). In a perpendicular field, ρ was almost doubled (from A′ to B′). these changes were reversible, since the magnetoresistance returned to the initial values (A and A′) after the vacuum of the experimental instruments was broken and the samples were oxidized in air.

The results for molybdenum (d = 0.15 mm) are shown in Fig. 2, where segments AB and A′B′ denote the corresponding changes in a magnetic field parallel and perpendicular to the surface, respectively. The general tendency, as seen from Fig. 2, remains the same as for tungsten, but the extent of this change is smaller, namely, in a parallel field the magnetoresistance decreased to approximately one-half and in a perpendicular field it increased by 10%.

Figure 4 shows curves describing the change of the magnetoresistance of a tungsten plate (d = 0.06 mm) with an atomically pure surface, after a measured amount of impurity were deposited on it. The measurements were made in a magnetic field of 10 kOe. It is seen from the figure that an increase in the concentration of the oxygen in the adsorbed state leads to an increase in the crystal resistance in a parallel magnetic field (curve 1) and to a decrease in the perpendicular field (curve 3). Both plots exhibit saturation at identical oxygen concentration, corresponding approximately to two monatomic layers, and have singularities that appear when the first layer is filled. The concentration dependence for silver, measured under the same conditions in a parallel magnetic field, is shown by curve 2 of Fig. 4. The singularity in the form of a smeared-out minimum is likewise apparently connected with the completion of the first atomic layer of the silver film, and is quite distinctly seen here. Annealing to room temperature, and probably certain ordering of the structure of this layer, made the minimum deeper (dashed curve).

The results for molybdenum are shown in Fig. 5. Curves 1 and 2 were measured at different rates of oxygen deposition (the pressures in the source were 2×10^{-6} and 9×10^{-7} mm Hg). It is seen from the figure that the adsorption of the oxygen led to an increase of the magnetoresistance of the crystal in a parallel field (by 85%) and to a decrease in a perpendicular field (by 8%).

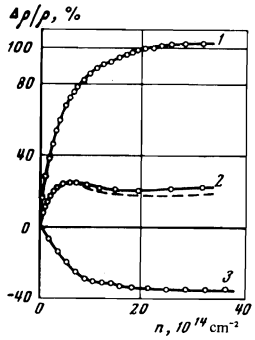

FIG. 4

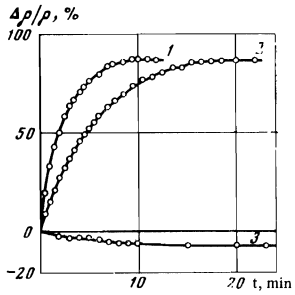

FIG. 5

FIG. 4. Relative change of magnetoresistance of a tungsten crystal, d = 0.06 mm, in a constant magnetic field of 10 kOe as a function of the surface concentration of the foreign matter. Curves 1 and 3–in the course of adsorption of oxygen (1–in field $\mathbf{H} \perp \mathbf{n}$; 3–in field $\mathbf{H} \parallel \mathbf{n}$), 2–in the course of adsorption of silver in a field $\mathbf{H} \perp \mathbf{n}$.

FIG. 5. Relative change of magnetoresistance of molybdenum crystal, d = 0.15 mm, in a constant magnetic field 10 kOe during the course of adsorption of oxygen. Curves 1 and 2–in fields $\mathbf{H} \perp \mathbf{n}$ at pressures in source 2×10^{-6} and 9×10^{-7} mm Hg, 3–in field $\mathbf{H} \perp \mathbf{n}$ at a pressure at a pressure 9×10^{-7} mm Hg.

In all cases, cleaning the surface returned the magnetoresistance to the initial values (points B and B′ in Figs. 1 and 2).

The plate resistance, measured as a function of the intensity of the magnetic field at various combinations of sample thickness, field orientations, and degrees of surface finish, followed a quadratic law, which was well satisfied in fields H > 2 kOe.

DISCUSSION OF RESULTS

Let us discuss the applicability of the model of the static skin effect to the relations observed here. Within the framework of this model, allowance for the collisions of the electrons with the crystal boundary leads to the following asymptotic expressions.

In a parallel magnetic field

$$\sigma_{\parallel} = a\sigma_0 \frac{\gamma}{q+\gamma}\frac{r}{d} + \sigma_0\gamma^2, \quad \mathbf{H}\perp\mathbf{n}. \tag{1}$$

Application of the theory to the case of a perpendicular field yields

$$\sigma_{\perp} = b\sigma_0 q\gamma \frac{r}{d} + \sigma_0\gamma^2, \quad \mathbf{H}\parallel\mathbf{n}. \tag{2}$$

Here σ_0 is the conductivity without the magnetic field, σ is the average conductivity of a thin plate, a and b are factors of the order of unity, q = 1 − p, p is the specularity coefficient. The first terms in the right-hand sides of the equations take into account the surface conductivity.

Let us formulate briefly the conclusions that follow from an analysis of these equations.

1. In a sufficiently strong magnetic field ($q \gg \gamma$), for diffused reflection from the walls (q = 1), the surface conductivities in Eqs. (1) and (2) agree, apart from the factors a and b, and the size effect appears at all orientations of the magnetic field. We note that the currents at the conductor boundary, in fields $\mathbf{H} \perp \mathbf{n}$ and $\mathbf{H} \parallel \mathbf{n}$, are formed by electrons corresponding to different sections of the Fermi surface. For this reason, $\sigma_{\parallel}$ and $\sigma_{\perp}$ depend on the singularities in the shape of the Fermi surface and in the general case we have $a \neq b$.

2. With increasing specularity of the reflections, the surface conductivity in a parallel magnetic field increases; in a perpendicular field it decreases, and drops to zero in the limit q = 0. These regularities are based on a simple physical cause. Indeed, the surface current at $\mathbf{H} \perp \mathbf{n}$ is determined by electrons that move in a thin layer, on the order of r, at the boundary and collide with the surface. Regardless of the character of the scattering, their mobility is higher than in the volume of the conductor. In the case of specular reflection, the correlation between the incident and reflected electrons ensures optimal conditions for carrier drift along the surface. To the contrary, in a perpendicular field $\mathbf{H} \parallel \mathbf{n}$, the most mobile are the electrons that experience diffuse reflection from the surface. In each such collision, the axes of the helical trajectories were described by the electron in the magnetic field shift in the plane of the plate by an amount on the order of r. Striking the specular surface does not change the axis of the trajectory, and the presence of the surface does not manifest itself at all in this case.

3. The dependence of the electric conductivity (or of the resistivity) on the magnetic field under the condition $q \gg \gamma$ and at all orientations of **H** is the same as in a bulky sample. An exception is the case q = 0, which is apparently never realized in experiment, and in which the conductivity in a parallel field is a linear function of H.

Thus, the analysis presented here allows us to assume that all the relations observed in experiments with thin plates of tungsten and molybdenum can be explained within the framework of the static skin-effect model. Assuming this model and using Eqs. (1) and (2), we can estimate the value of p. We note immediately that for real surfaces that become contaminated in air these estimates are only qualitative. An exact calculation is certainly useless here, since Eqs. (1) and (2) contain the parameters a, b, and l, the values of which are known only approximately. Nonetheless, to explain the size-effect relations, particularly the relation measured in a perpendicular field (see Figs. 1–3), we must assume that the crystal surfaces scatter the electrons almost diffusely. This conclusion agrees with the widely held point of view and is confirmed by a number of experiments, e.g.[6].

Cleaning the surface in vacuum leads to significant changes in the conductivity of the plates. The fact that these changes are reversible or can result from adsorption indicates that this is a purely surface effect and is the result of the change in the character of the reflection of the electrons from the boundary. Using this, we can estimate the limits of the variation of the specularity coefficient and, in final analysis, to determine its value for the cleaned surface. Estimates of this kind were made earlier for tungsten in a parallel field, and it was established that an atomically pure surface can reflect electrons with a high degree of specularity (p = 0.7–0.8)[5].

We use the same procedure to calculate p in a perpendicular field. To this end we rewrite Eq. (2) in the form

$$p = 1 - \frac{1/\rho(2) - 1/\rho_\infty}{1/\rho(1) - 1/\rho_\infty} \tag{3}$$

Here ρ_∞ is the magnetoresistance of the bulky plate, and $\rho(1)$ and $\rho(2)$ are the magnetoresistances of the

thin plates before and after cleaning the surface. Assuming that on the real, uncleaned surface we have $p = 0$ and $\rho_\infty = 2.5 \times 10^{-6}$ Ω-cm for W with a ratio $\rho(300°K)/\rho(4.2°K) = 33 \times 10^3$ and $\rho_\infty = 4.1 \times 10^{-7}$ Ω-cm for Mo with a ratio 20×10^3, we obtain specularity coefficients $p = 0.8$ and $p = 0.2$ for atomically pure surfaces of tungsten and molybdenum, respectively.

Calculations performed for the case of a parallel field using Eq. (2) of[5] yield $p = 0.8$ and $l = 1.2$ mm for tungsten and $p = 0.6$ and $l = 0.3$ mm for molybdenum. For tungsten, different methods yield results that agree well. There is no such agreement for molybdenum.

Thus, the imperfections of the structure and contaminations of the surface destroy the coherence of any incident wave packet and decrease the diffuseness of the reflection of the electrons from the crystal boundary. Cleaning the surface restores the natural symmetry of the surface structure and increases the specularity of the reflection. In this sense, the analogy with transport phenomena in the volume of the crystal are complete in this case.

[1] V. G. Peschanskiĭ and M. Ya. Azbel', Zh. Eksp. Teor. Fiz. 55, 1980 (1968) [Sov. Phys.-JETP 28, 1045 (1969)].
[2] A. F. Andreev, Usp. Fiz. Nauk 105, 113 (1971) [Sov. Phys.-Uspekhi 14, 609 (1972)].
[3] R. F. Grin, in: "Poverkhnostnye svoĭstva tverdykh tel" (Surface Properties of Solids), Mir, (1972), p. 127.
[4] O. A. Panchenko and P. P. Lutsishin, Zh. Eksp. Teor. Fiz. 57, 1555 (1969) [Sov. Phys.-JETP 30, 841 (1970)].
[5] P. P. Lutsishin, O. A. Panchenko, and A. A. Kharlamov, Zh. Eksp. Teor. Fiz. 64, 2148 (1973) [Sov. Phys.-JETP 37, 1083 (1973)].
[6] A. P. Perov, Zh. Eksp. Teor. Fiz. 63, 1324 (1972) [Sov. Phys.-JETP 36, 699 (1973)].

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