Effect of electron-hole transfers on the static skin effect in tungsten crystals

O. A. Panchenko, A. A. Kharlamov, and Yu. G. Ptushinskiĭ

Physics Institute, Ukrainian Academy of Sciences
(Submitted March 13, 1974)
Zh. Eksp. Teor. Fiz. **67**, 780–787 (August 1974)

The case is considered when a Bloch wave specularly reflected from a metallic surface corresponds to several states being located on different sheets of the equal-energy surface. Depending on the shape, sign of Gaussian curvature, and mutual position of the sheets of the equal-energy surface, and also on the orientation of the crystal physical boundary, these reflections can cause the tangential components of the electron group velocity before and after the "specular" reflection to be sometimes of opposite sign. Such reflections can occur in tungsten cyrstals from the (100) and (111) faces but are impossible from the (110) face. In this connection a comparative investigation was carried out of the nature of conduction-electron reflection from atomically pure or oxidized (100) and (110) faces of a tungsten single crystal. The measurements were performed at liquid-helium temperatures with thin ($l \gg d$) plane-parallel plates cut from a very pure bar with a ratio $\rho_{300\,°K}/\rho_{4.2\,°K} = 20\times10^3$. It is found that the atomically pure (100) face is almost diffuse whereas the (110) face reflects conduction electrons with a high degree of specularity. The character of the conduction-electron reflection from the metallic surface is investigated by the static-skin-effect method.

Until recently, the metal-vacuum interface was usually regarded as an accumulation of random inhomogeneities and crystal-structure defects. It was therefore assumed that the reflection of the conduction electrons from a real metal surface is predominantly diffuse. Nonetheless, investigations of the principal faces of single crystals of high-melting point metals, from which the oxides and carbides were removed by high-temperature heating and which were stored under conditions of ultrahigh vacuum, give grounds for assuming that the upper layers of the atoms form sufficiently ordered structures and are arranged in practically the same order as in the volume of the metal. Such atomically-smooth and pure surfaces constitute unique two-dimensional diffraction gratings, which reflect coherently both the conduction electrons and the electrons incident on the crystal from the vacuum. This makes possible specular reflection of the conduction electrons, or else formation of the diffraction pattern on the screen of an electronograph.

An analysis carried out by Andreev and Green[1,2] has shown that specular reflection(meaning reflections with conservation of the tangential component of the electron quasimomentum $\mathbf{k}_{\parallel}$) is possible when the surface grating has a natural translational symmetry, which is peculiar to the given direction in the crystal. To the contrary, the absence of order or violation of the symmetry leads to diffuse reflection. This leads to the natural assumption that observation of a diffraction pattern corresponding to natural symmetry of some crystal face is sufficiently definite evidence that the reflection of the carriers from this surface should be predominantly specular ($k_{\parallel}$ = const).

It should be noted, however, that a specular reflection of a Bloch wave does not always correspond to conservation of the tangential component of the velocity $\mathbf{v}_{\parallel}$ of the electron. Indeed, only in metals with isotropic Fermi surface do the directions of the group-velocity vector $\mathbf{v}$ and of the quasimomentum of the electron $\mathbf{k}$ coincide at all orientations. In metals with anisotropy, especially a multi-sheeted Fermi surface, an incident Bloch wave can lead to the appearance of several reflected waves, depending on the form or on the mutual disposition of the individual sheets of the equal-energy surface and on the orientation of the physical boundary of the crystal. For certain directions, these peculiarities of the reflection cause the tangential components of the electron velocity before and after the "specular" reflection to be opposite to each other; in this case the crystal boundary, which is specular in the sense of the reflection of a Bloch wave, can be in essence diffuse. In tungsten, for example, such singled-out directions are in the axes ⟨100⟩ and ⟨111⟩; for this reason, the faces (100) and (111) can be diffuse (the face (110) remains specular).

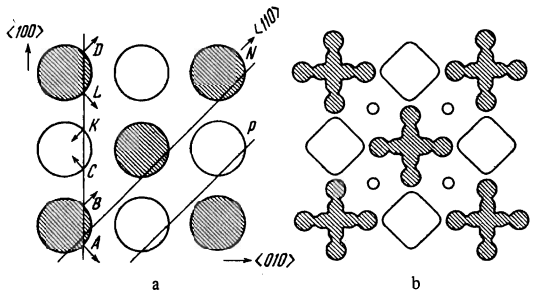
The present paper is devoted to a comparative investigation of the character of the reflection of conduction electrons from the faces (100) and (110) of single-crystal tungsten. Both atomically-pure surfaces give well-observable diffraction patterns belonging to the natural symmetry of these planes[3,4], and can therefore be assumed to be specular for the reflection of Bloch waves; the second, as shown earlier[5,6], indeed reflects conduction electrons almost specularly.

To produce a crystal surface that is certainly diffuse, oxygen was adsorbed in certain cases. The character of the reflection of the conduction electrons from the metal boundary wave investigated by the static skin effect method[7].

THE MODEL

To clarify the situation of interest to us, we consider the schematic model of an equal-energy surface constructed in such a way that closed surfaces, say spheres, having equal dimensions but opposite signs of Gaussian curvatures, are arranged in the ⟨100⟩ direction and alternate with a period equal to the reciprocal lattice. Arranged in checkerboard order, they occupy all of reciprocal space. One of them corresponds to electronic states and the other to hole states (for the sake of clarity, the electronic surfaces are shown shaded in Fig. 1).

Consider the reflection of a conduction electron from the (100) face[1]. Let the wave incident on the surface of the crystal correspond to point A of phase space, located on the "electronic" sphere (Fig. 1a). Using the conservation of the energy and of the tangential component of the quasimomentum, and recognizing that the quasiparticle momentum is determined only accurate to within the reciprocal-lattice vector $\pm 2\pi\hbar b$, let us determine the possible states of the reflected electron. They



a b

FIG. 1. Topology of the Fermi surface of tungsten: a—idealized model; b—model constructed in accordance with the data of [8].

are located on all the equal-energy surfaces at the points where the surfaces intersect the line $\mathbf{k}_{||}$ = const, drawn from A, i.e., at the points B, C, D, etc. The states K and L correspond to velocities directed from the surface to the vacuum. It follows therefore that the reflected wave can produce two types of states, situated on the electronic (B, D . . .) or hole (C . . .) surfaces. In symmetrical cases we can confine ourselves to consideration of the states B and C, which are realized with relative probabilities W_1 and W_2 (for which, naturally, $W_1 + W_2 = 1$).

It is important to note that transitions of the type A → B leave the electron tangential velocity unchanged; to the contrary, transitions of the type A → C, which are accompanied by conversion of an electron into a hole and consequently reverse the sign of the carrier effective mass, lead to a change of the tangential velocity of the particle (Fig. 2). The scattering of holes by the (100) surface naturally follows the same rules.

We consider now reflection from the (110) face. The lines $\mathbf{k}_{||}$ = const are oriented in this case along the ⟨110⟩ axis and intersect only electron or only hole surfaces. For this reason, no conversion of quasiparticles into each other takes place on this face. For a quantitative treatment of this phenomenon, it is undoubtedly important to determine the ratio of W_1 and W_2. For "good" metals, the traditional notion is that the times of the interband and intraband relaxation are of the same order ($\tau_1 \sim \tau_2$). Assuming that this is correct, also in the case of scattering by a surface, we can conclude that $W_1 \sim W_2 \sim 0.5$. We shall discuss this assumption later on.

Let us examine, bearing in mind the static skin effect, the consequences ensuing from the interband scattering considered here. As is well known, in the presence of a strong magnetic field ($\gamma \ll 1$, where $\gamma = r/l$, r is the Larmor radius, and l is the carrier mean free path), the interaction between the electrons and the crystal boundary leads to a redistribution of the current over the conductor cross section, and to a concentration of the current at the surface, where the electron mobility in some cases turns out to be much larger than in the volume. This phenomenon is called the static skin effect[7]. In plane-parallel plates, the cases when the magnetic field is oriented in the plane of the plate or is directed normal to it are fundamentally different (we have here $\mathbf{H} \perp \mathbf{j}$ throughout, where j is the current direction). Let us consider these cases separately.

In a parallel magnetic field, the surface current is determined by electrons moving in a thin layer of dimension r near the conductor boundary, and colliding with the surface. Regardless of the character of the reflection (diffuse or specular), their mobility is higher

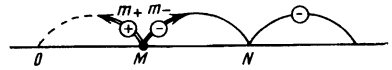


FIG. 2. Carrier trajectory at metal-vacuum interface. An electron is converted into a hole at the point M.

than in the volume of the metal. In the case of specular reflection, the correlation of the incident and reflected electrons ensures optimal conditions for carrier drift along the surface. Their drift length is limited in this case only by the value of l. In diffuse reflection, the mean free path is much shorter and equal to the distance between two successive impacts against the surface, i.e., to r. Inclusion of the interband transitions on the specular surface alters significantly the character of the carrier drift on the boundary, namely, depending on the type of transition A → C or A → B) realized in each concrete act of collision with the surface, the carrier can be located at the preceding starting point A or can proceed to the point N. If $W_1 = W_2$, the forward and backward "steps" are equally probable and the motion of the electron drifting at the surface should obey the laws of Brownian motion. In this case the mean free path is equal to r and consequently the experimentally measured diffuseness coefficient q should be equal to unity.

In a perpendicular magnetic field, the most mobile are the electrons experiencing diffuse reflection from the surface. In each such collision, the axes of the helical trajectories described by the electron in the magnetic field shifts in the plane of the plate by an amount on the order of r. Impact against the specular surface does not change the position of the current tube, and the presence of the surface does nothing in this case. Inclusion of the interband transitions likewise does not change the positions of the current tube in space when the carriers collide with the sample boundary; all that changes is the direction of their rotation in the magnetic field. Thus, interband transitions do not manifest themselves in a perpendicular field, and the surface remains effectively specular.

We note in conclusion that the analysis presented here was carried out within the framework of an idealized model, namely, it was assumed that the energy surfaces are spherical cavities. For tungsten, naturally, this idealization is only a rough approximation, since the hole surface and all the more the electron surface have complicated topologies. This is seen in Fig. 1b, which is constructed from the data of[8]. This complicates somewhat the general picture of the phenomenon: 1) we can no longer assume that the electron and hole states situated on one straight line $\mathbf{k}_{||}$ = const always correspond to equal Larmor radii r; 2) transitions of type A → C (or K → B), do not always lead to an exact reversal of the direction of the tangential velocity component. These features should complicate the quantitative calculation of the phenomenon, which was considered above with a simple model as an example, but nonetheless cannot change its qualitative aspect.

EXPERIMENTAL PROCEDURE

In general outline, the experimental procedure does not differ from that described earlier[5]. The measurements were performed at liquid-helium temperature with samples oxidized in an oxygen atmosphere or in

air, or else purified and stored in high-vacuum (10^{-11} mm Hg). The samples were rectangular plates measuring 6 × 2 mm and were cut from a blank of high purity with ratio $\rho_{300°K}/\rho_{4.2°K} = 20 \times 10^3$. The samples were oriented in the planes of the faces (100) and (110) accurate to within 10 minutes of angle. The current flowed in the ⟨100⟩ direction. The plate surfaces were ground and treated in an electrical polishing solution to mirror brightness, and the crystals were cleaned in vacuum at high temperature by the standard procedure described by Stern[3]. We note that tungsten crystals reduced by this technology give well-observable pictures of slow-electron diffraction.

The construction of the sealed glass vacuum device was described in detail earlier[5]. The samples were mounted in such a way that their principal axes coincided with the axis of the experimental vacuum tube immersed in a helium cryostat. This has made it possible, by rotating the tube between the poles of an electromagnet, to investigate the angular dependences of the magnetoresistance of the plates with oxidized and with atomically-pure surfaces. The oxygen source was placed in the "warm" part of the vacuum instrument, located outside the cryostat. The oxygen was evaporated from a heated platinum tube filled with copper oxide. Thermal decomposition of the oxide increased the pressure in the experimental instrument to 10^{-6}–10^{-5} mm Hg. When necessary, the oxygen was pumped out with a titanium pump.

In all cases, the final purification of the crystals was carried out already in the cryostat with the helium port in. The samples were heated for a short time to 2500°K. As a result of this procedure, a film of adsorbed matter was evaporated from the surfaces of the crystals, settled on the crystal from the atmosphere of the residual gases, and influenced strongly the state of the surface.

The measurements were performed in an electromagnet at a field intensity 8.9 kOe. The sensitivity of the measuring potentiometer circuit was 10^{-7} eV.

EXPERIMENT

The results of the measurements of the angular dependences of the magnetoresistance for thin (d = 0.08 mm) plates of tungsten oriented parallel to the two principal faces (100) and (110) of the single crystal are shown in Fig. 3. The parameter of the curves is the concentration of the oxygen surface impurity, which ranged from 0 to $\sim 10^{15}$ cm^{-2}. The magnetoresistance ρ_∞ of the bulk crystals, measured with the magnetic field oriented along ⟨100⟩ and ⟨110⟩, was 8.2×10^{-7} and 1.1×10^{-6} Ω-cm, respectively.

Figure 3 shows the following:

1) At all orientations of the magnetic field, the magnetoresistance of the thin plates is less than the magnetoresistance of the bulk samples. The size effect becomes most clearly manifest in a parallel magnetic field (this orientation in Fig. 3 corresponds to zero angle).

2) Evaporation of the oxide film leads to a growth of the magnetoresistance in a perpendicular field and to a decrease in a parallel field. In the perpendicular field, the relative changes $\Delta\rho_\perp/\rho_\perp$ for the two plates are comparable in magnitude and amount to 25 and 18% for the plate with (100) and (110) face, respectively. In a parallel magnetic field, the relative changes $\Delta\rho_\parallel/\rho_\parallel$ are significantly different for crystals oriented along different faces, namely, in the former case the change is only 19% and in the latter 450%.

The dynamics of the variation of the magnetoresistance with time following adsorption of oxygen in a constant stream is shown in Fig. 4. The measurements were made in a parallel magnetic field on two crystals of equal thickness (d = 0.1 mm), oriented along the faces (100) and (110) and placed in a single experimental instrument. The adsorption of oxygen (which took place in this case on the side of the plate facing the source) led to an increase of the magnetoresistance $\Delta\rho_\parallel/\rho_\parallel$(100) by ~3–4% and $\Delta\rho_\parallel/\rho_\parallel$ (110) by 100%. Desorption returned the magnetoresistance of the plates to the initial values.

DISCUSSION

Let us formulate briefly the conclusions that can be drawn from the analysis of the model considered above: in a parallel magnetic field, allowance for the interband transitions increases the effective diffuseness of the faces (100) and (111). The third principal face (110) of the tungsten crystal remains specular. In a perpendicular field, no interband transitions appear. All principal faces can become specular. As seen from Figs. 3 and 4, the predicted difference is indeed observed in experiment. Thus, oxidation of an atomically pure (100) surface results in a parallel field in only small changes of

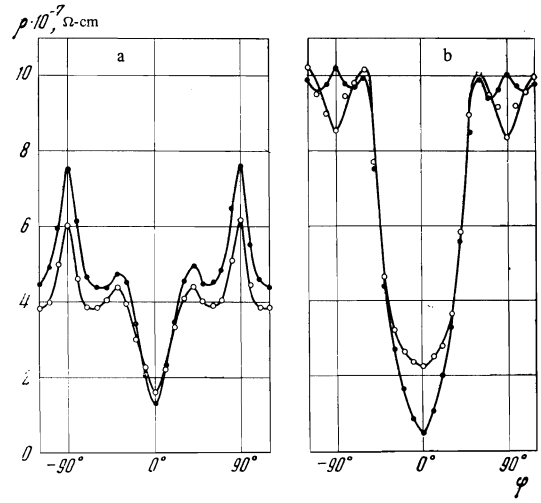


FIG. 3. Angular dependences of the magnetoresistance $\rho(\varphi)$ at H = 8.9 kOe for tungsten plates oriented parallel to the faces (100) (a) and (110) (b): ○–oxidized surface, ●–atomically pure surface.

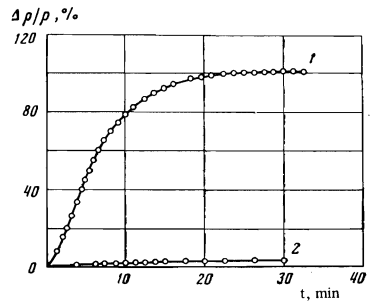


FIG. 4. Relative changes of the magnetoresistance of thin (d = 0.1 mm) tungsten crystals in a constant magnetic field 8.9 kOe as a function of the oxygen evaporation time: 1–(110) face, 2–(100) face. The magnetic field is oriented parallel to the surface.

the magnetoresistance of a thin plate. This fact can be naturally explained by assuming that the atomically pure face (100) scatters the conduction electrons almost diffusely (it is postulated here, of course, that the oxidation of the surface leads to complete or almost complete diffuseness, which results from violation of the periodic potential relief of the surface).

Using the data presented in Fig. 3 and assuming that p = 0 on the oxidized surface (here p is the specularity coefficient, let us estimate p for an atomically pure surface (100) in parallel and perpendicular magnetic fields. For the (110) face, these estimates were made earlier (see[5,6]), and it was found that $p_{\parallel} = p_{\perp} = 0.8$. Allowance for the boundary effects in a strong magnetic field[7] leads to the following simple expressions, which are convenient for calculation of p and l.

In a parallel magnetic field

$$\rho_{\parallel}=\rho_{\infty}\frac{(1-p)d}{l+(1-p)d}, \quad p_{\parallel}=1-\frac{\rho(2)}{\rho(1)}. \tag{1}$$

These expressions are valid at $l \gg d$ and $1 \gg \gamma$.

In a perpendicular magnetic field

$$p_{\perp}=1-\frac{1/\rho(2)-1/\rho_{\infty}}{1/\rho(1)-1/\rho_{\infty}}. \tag{2}$$

Here $\rho(1)$ and $\rho(2)$ is the magnetoresistance of a thin plate before and after purification of the surface.

The use of formulas (1) and (2) yields for the (110) face $p_{\parallel} = 0.8$ and $p_{\perp} = 0.8$; for the (100) face we get $p_{\parallel} = 0.2$ and $p_{\perp} = 0.8$ (the mean free path l for both plates is 0.5 mm, so that actually $l \gg d$, and the quantity γ satisfies the relation $1 \gg \gamma$ in fields ~10 kOe).

It is important to emphasize that $p_{\parallel}$ measured on different faces of one and the same crystal turned out to be significantly different, namely 0.2 for (100) and 0.8 for (110). This difference can be attributed to interband transitions that are realized on the (100) face with a high probability, equal to ~0.5.

In a perpendicular magnetic field, the values of $p_{\perp}$ coincide for different faces, and this shows that the results obtained in a parallel field for the (110) face are not trivial.

[1)] A similar analysis was presented by Andreev [1] for a system of equivalent equal-energy surfaces.

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Translated by J. G. Adashko
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