Reflection of conduction electrons from an atomically pure (110) face of a tungsten crystal

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(Submitted November 30, 1972)
Zh. Eksp. Teor. Fiz. **64**, 2148-2153 (June 1973)

The nature of the reflection of conduction electrons from an atomically pure (110) tungsten crystal face covered with a monatomic oxygen film is studied by the static skin effect method. A high degree of specularity of the reflection from the atomically pure surface is observed. The interpretation of this result is based on Andreev's theory, according to which the reflection of Bloch waves incident on the surface may be coherent if the physical surface is parallel to one of the crystallographic planes and its atoms retain the natural translational symmetry of the crystal. Adsorption of oxygen results in the violation of coherency and in an increase of the diffusivity.

INTRODUCTION

For a number of phenomena in metallic samples of finite dimensions, the character of the interaction of the electrons with the boundaries of the sample turns out to be significant. This is most apparent in perfect crystals at low temperatures, when the mean free path increases to values that are commensurate with the current-carrying regions of the conductor. Usually, this interaction is described by the phenomenological parameter p, which determines the fraction of electrons reflected specularly or diffusely $(1-p)$.

In the current literature, it has been rather firmly established that the reflection of electrons from the surface of metals is practically diffuse. The opinion is based on the fact that the length of the probability wave of the conducting electrons is commensurate with the interatomic distances and is the same as the dimensions of the roughness of the potential relief of the surface. This is indicated, for example, by the repeatedly observed increase in the resistivity in thin metallic films and by experiments on the anomalous skin effect,[1] and also by a number of other experimental results.[2] Electrons in semimetals[3] and glancing electrons[4] are exceptions. For the former, the specularity is due to the large wavelength, and for the latter to the large effective wavelength in the direction perpendicular to the surface.

It should be noted that the existing experimental data refer only to real surfaces and not to any that have been subject to any sort of special treatment and purification. Such surfaces are always covered by a film of adsorbed material or oxide and can have distortions in structure. At the same time, there is a basis for assuming that reflection in metals can take place rather specularly under the condition that the surface preserves the natural translational symmetry of the crystal, is not covered by foreign atoms, and is identical with one of the crystallographic planes.[5] In this connection, we carried out an investigation of the character of the reflection of electrons from an atomically pure (110) face of a tungsten single crystal.

The measurements were carried out by the static skin-effect method, the mechanism of which consists in the following:[6] the magnetic field decreases the mobility of the carriers in the volume of the conductor (according to the law $\mu \sim H^{-2}$ in metals with equal concentrations of electrons n_1 and holes n_2) and almost does not change it for surfaces oriented parallel to the field. Under these conditions, the change in the state of the surface brought about by cleaning, adsorption of foreign atoms, or their desorption materially affects the conductivity of the crystal and can be observed experimentally.

METHOD OF EXPERIMENT

The investigations were carried out under high-vacuum conditions (10^{-11} mm Hg) in sealed-off apparatus on single crystal samples of high-purity tungsten with a resistance ratio $\rho(300^\circ\text{K})/\rho(4.2^\circ\text{K} \approx (20-25) \times 10^3$.

A general view of the experimental apparatus is shown in Fig. 1. The sealed-off glass vacuum apparatus 1 was immersed in a helium cryostat 2 that had been adapted for magnetic measurements. The vacuum apparatus was equipped with a manometer 3 for measurement of very low pressures, an adsorption-cooled titanium pump 4, and an adsorbate source 5. These systems were placed outside the helium cryostat. A heated platinum tube filled with copper oxide served as the adsorbate source. Decomposition of the copper oxide released oxygen. A quality of the source was checked with a mass spectrometer.

Tungsten crystals in the form of thin plates with dimensions $8 \times 2 \times 0.1$ mm with lugs for electrical contacts (see Fig. 1, insert) were cut from the single-crystal bar with a spark cutter. Final finishing and lapping to the proper thickness were carried out by an electrochemical method. This made it possible to remove the surface-defect layer which develops upon cutting and polishing the crystal.

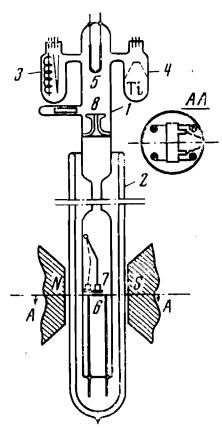

FIG. 1. Overall view of the experimental apparatus: 1 – vacuum system, 2 – helium cryostat, 3 – manometer, 4 – titanium pump, 5 – oxygen source, 6 – tungsten crystal, 7 – electron gun, 8 – vacuum valve, insert – mounting of sample.

The sample 6 under study was located in the tube of the vacuum apparatus in the manner shown in Fig. 1 (insert). The crystal was suspended by two tungsten wires of diameter 100 μ, electrically welded to the ends of four sufficiently elastic molybdenum cross arms of diameter 1.5 mm. Such a construction made it possible to maintain a rather homogeneous temperature of the sample during heating and reduced mechanical stresses to a minimum. The surface of the sample was rid of the carbon compounds, which are always present in tungsten in small quantities and which contaminate the surface, by baking the plates in an oxygen atmosphere at a pressure of 10^{-5} mm Hg for 10 hours. The heating of the crystal to the temperature of 2500°K, which was necessary for this purpose, was achieved by passing an electric current. A movable electron gun was mounted in the immediate vicinity of the crystal; this was intended for the measurement of the work function of the investigated surface. These measurements were necessary as a control on the purity of the initial surface and for estimates of the surface concentration of the adsorbed oxygen. The movable gun was furnished with a small magnet, which shunted the gun to the side of the crystal when the magnetic field was turned on. The oxygen was evaporated on the cooled, clean surface of the crystal immediately before the experiment. There was no direct control of the temperature of the sample during the evaporation and the measurements. It was assumed that it was close to the temperature of the liquid helium. A ground-glass vacuum valve 8 was included in the experimental apparatus, to shut off the flow of oxygen to the sample. The valve, controlled by an external magnetic, was closed during reading of the experimental data. After completing a regular cycle of measurements, we cooled the oxygen by means of the titanium pump and cleaned the crystal by a series of short-duration heatings. The measurement cycle was repeated a number of times. The measurements were carried out in magnetic fields up to 10 kOe. The sensitivity of the measuring null-balance circuit was never less than 10^{-7} V.

EXPERIMENTAL RESULTS

Figures 2 and 3 give the data characterizing the measurements of the magnetoresistance of the plate in a parallel magnetic field for different treatments of the surface. Curve 1 of Fig. 2 gives in logarithmic scale the ρ(H) dependence for a plate etched in an electropolishing solution. These measurements were carried out in air. Curve 2 of the same drawing gives the ρ(H) dependence for a crystal purified by heating in high vacuum. It is seen from the graph that the cleaning of the surface leads to a significant decrease in the magnetoresistance of the crystal. The magnetoresistance of the plate in a perpendicular field was somewhat increased upon cleaning of the crystal (curves 6 and 7). Repeated etching increases the magnetoresistance of the plate for both directions of the field relative to the initial value.

The adsorption of oxygen on the clean surface led to an increase in the resistance. Curves 3, 4 and 5 of Fig. 2 show successive stages of this process. The results of the investigation of the effect of the adsorption on the resistance as a function of the evaporation time (or the concentration) in a constant magnetic field of 10 kOe oriented parallel to the surface are given in Fig. 3. The oxygen was evaporated on the surface of the crystal in a molecular flow regime; and was adsorbed by the side of the plate facing the source. Tentative measurements of

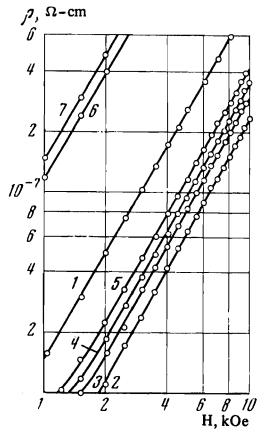

FIG. 2.

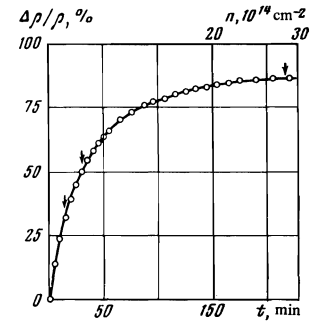

FIG. 3.

FIG. 2. Dependence of the resistivity of the crystal on the magnetic field intensity, oriented parallel to the surface of the plate: 1 – for a real suface; 2 – for a surface cleaned in a vacuum; 3, 4, 5 – for a surface covered with atoms of oxygen; 6 and 7 – for a magnetic field oriented perpendicuar to the surface (6 – before cleaning, 7 – after cleaning).

FIG. 3. Relative change in the resistance of the crystal in a constant magnetic field of intensity of 10 kOe (field directed parallel to the surface) during adsorption of oxygen. The arrows indicate the positions at which the ρ(H) dependence was measured for curves 3, 4, and 5 of Fig. 2.

the surface concentration show that the plot of $\Delta\rho/\rho$ against n flattens out when a coating corresponding to about a monolayer of oxygen atoms is produced. "Flash" evaporation of the oxygen by heating of the crystal to a temperature of 2500°K returns the resistance of the crystal to the original value.

DISCUSSION OF RESULTS

As follows from the plots in Figs. 2 and 3, the magneto-resistance of thin tungsten plates depends substantially on the state of the surface. This allows us to estimate the limits of change of the coefficient of specular reflection and, in the final analysis, to elucidate the value of this quantity for a clean surface.

Allowance for boundary effects in a strong magnetic field oriented parallel to the surface leads to the following expression for the conductivity of a thin plate:[6]

$$\sigma_{11} = \sigma_0 \frac{\gamma}{(1-p)+\gamma} \frac{r}{d} + \sigma_0 \gamma^2; \qquad (1)$$

here σ_0 is the conductivity of the bulk metal in the absence of a field; $\gamma = r/l$, where r and l are the Larmor radius and the free path length. The surface conductivity (the first term in the right side of (1)) arises from the reflection of electrons from the boundaries and is larger the higher the specularity p of the reflection. The conductivity in the volume (the second term) falls off as usual with increase in the magnetic field, according to a quadratic law. Investigations[7] of the static skin effect in tungsten have established that even in fields of 10 kOe the current density in the surface, in a layer of the order of the Larmor radius, is greater by an order of magnitude than the current density in the volume of the conductor. As a result, the resistance of plates in fields that are perpendicular and parallel differ substantially and, in thin films (d = 100 μ) the difference increases by 10–12 times. We note in passing that for this same reason, the state of the surface in a perpendicular field

should not affect the conductivity as much as in the parallel field. This is confirmed experimentally (see Fig. 2, curves 6 and 7).

It was shown in[6] that the character of the interaction of carriers with the surface determines the law of change of the resistance in a magnetic field oriented parallel to the surface. In the extreme cases of specular (p = 1) or diffuse (p = 0) reflection, the resistance is respectively a linear or a quadratic function of the magnetic field (for metals with $n_1 = n_2$). For intermediate cases ($0 < p < 1$) the quadratic law is satisfied only in a sufficiently strong magnetic field, under the condition that $(1-p) \gg \gamma$. It is seen from the plots of Fig. 2 that this condition is already satisfied at $H > 2$ kOe; here the expression (1) simplifies and reduces to a form which convenient for estimate of p:

$$\rho_{\parallel} = \rho_{\text{bulk}} \frac{(1-p)d}{l+(1-p)d}, \qquad (2)$$

where $\rho_{\parallel} = 1/\sigma_{\parallel}$ and $\rho_{\text{bulk}} = 1/\sigma_0\gamma^2$. We note that the estimate (2) is valid only for the intermediate case, where $0 \leq p < 1$, and is meaningless when p = 1.

It was shown in[7] that the static skin effect in tungsten is also determined to a considerable extent by carriers in small groups, which are scattered more specularly on the surface than the majority carriers. In this condition, the initial value of p for a contaminated surface can differ somewhat from zero. Nevertheless, for estimates of l and Δp, we neglect this fact and assume that p = 0 for a contaminated surface. In this assumption the mean free path calculated from (2) is $l \approx 1$ mm (in the calculations, it was assumed that $\rho_{\text{bulk}} = 7 \times 10^{-5}$ ohm-cm; this quantity was measured in a perpendicular field of 10 kOe at a sample thickness of d = 1 mm; under such conditions, the surface conductivity can be neglected). In this case the coefficient of specular reflection for the clean surface, as determined from Eq. (2), turns out to be equal to 0.7—0.8. We note that the error in the estimate of l does not have much effect on this final result. Large-scale roughnesses, which exist on a polished surface and which are visible in an optical microscope, increase the diffuseness of the scattering. It must be considered that reflection from an ideally smooth surface, having only irregularities of atomic scale, would have a still more specular character.

We emphasize that the changes in the resistance of the crystal, observed upon cleaning and adsorption of oxygen, are so great that they cannot be due only to a change in the character of the reflection of the electrons in small groups. We are undoubtedly dealing here with a sufficiently specular reflection of the majority groups of carriers, which have wavelengths that are comparable with the characteristic dimensions of the potential relief of the surface.

The possibility of such an interaction was predicted earlier by Andreev,[5] who showed that coherent reflection of the incident Bloch wave is possible in the case in which the physical surface is parallel to one of the crystallographic planes and its atoms are arranged in exactly the same way as in the body of the metal. In this case, the tangential components of the quasimomentum of the electrons are conserved in reflection. On the other hand, reflection from a random "irrational" cut of the crystal, which has no periodicity, cannot be coherent. Reflection of a beam of electrons incident on such a surface, for example, from a vacuum will likewise produce only a diffuse background.

In accord with these representations, the experimentally observed very significant effect of the treatment of the surface on the magnetoresistance of thin plates becomes understandable. Actually, it is well known that freshly prepared tungsten (110) surfaces do not produce a slow-electron diffraction pattern that is typical of this surface.[8] Such surfaces are covered with dilute solutions of carbon compounds that form microcrystals that endure heating to temperatures up to the melting point of tungsten. Only heating in an atmosphere of O_2 or H_2 leads to an effective carbon-free surface and to the establishment of its natural symmetry and, as a consequence, to an increase of the specularity. Subsequent adsorption of the oxygen by the clean surface again changes the position of the surface atoms, and disrupts the coherence of reflection from the two-dimensional diffraction lattice, and in final analysis, leads to an almost doubling of the resistance of the crystal. It is characteristic that, upon building up of the first atomic layer and the transition to the second, the $\Delta\rho/\rho = f(n)$ curve shows quite clearly a singularity associated with a new significant disruption of the periodicity of the potential of the surface (Fig. 3).

Thus reflection of conduction electrons from an atom atomically pure (110) face of tungsten can be quite specular; disruption of the natural structure of the surface even on an atomic scale leads to noticeable increase in the diffusivity.

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Translated by R. T. Beyer
228