Interaction between conduction electrons and the (110) face of a tungsten single crystal

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The (110) face of a tungsten single crystal purified in high vacuum retains the natural translational symmetry of the lattice along the mean direction at the crystal boundary. The reflection of conduction electrons from such surfaces is specular to a sufficient degree (the specularity coefficient p is estimated at 0.8–0.7). It is shown that a monoatomic tungsten film sputtered on a perfect (110) face of a tungsten crystal, which alters only the atomic arrangement on the sample surface, decreases the specularity coefficient considerably. Sputtering of copper, the first two or three atomic layers of which duplicate the structure of the substrate, leads to a periodic dependence of p on the copper concentration. It is concluded that the nature of the electron reflection depends on the symmetry at the crystal surface and changes when the type of diffraction processes at the boundary of the solid is altered. Data on the nature of electron reflection are obtained by investigating the static skin effect {V. G. Peschanskiĭ and M. Ya. Azbel', Zh. Eksp. Teor. Fiz. **55**, 1980 (1968) [Sov. Phys. JETP **28**, 1045 (1969)]}.

PACS numbers: 79.20.Kz, 81.20.−n

INTRODUCTION

Refractory-metal plates oriented in crystal-face planes with small Miller indices, purified and annealed under high-vacuum conditions, have surfaces that are in thermodynamic equilibrium and preserve the natural translational symmetry of the lattice along the average direction of the sample boundary. This is evidenced by numerous investigations recently performed by the slow electron diffraction (SED) method. These surfaces turn out to conform fully to those idealized models which make it possible to calculate the law governing the reflection of the conducting electrons. The results of an analysis of this kind, carried out by A. F. Andreev and R. F. Greene, [1,2] reduces briefly to the following.

All the conduction electrons incident on an ideal metal surface that lies in the symmetry plane of the crystal are reflected only specularly. By this is meant a reflection in which the tangential components of the electron quasimomentum are conserved, $k_{\parallel}^0 = \text{const}$. Lowering the symmetry on the crystal surface readily upsets the specular character of the reflections. The carriers can then be reflected into one of possible states characterized by an entire set of values. $k_{\parallel}^0, k_{\parallel}' \ldots k_{\parallel}^n$. The normal components of the quasi-momenta $k_{\perp}$ are determined by the points where all the straight lines $k_{\parallel}$ $= \text{const}$, drawn in reciprocal space, intersect all the equal-energy surface sheets $E(k) = \text{const}$. These laws are based on a simple physical cause, namely that in metallic crystal the wavelength of the electrons incident on an ideal boundary cannot be less than the distance between the equivalent sites of the two-dimensional lattice existing on the surface of the solid. For metals with closed Fermi surfaces this is obvious. As a result, the Bragg-reflection condition is never satisfied for ideal surfaces. To the contrary, when the symmetry is lowered in "good" metals, the inverse relation $\lambda < a$ is easily reached (a is the new period on the surface); as a result, diffraction reflections of the first and higher orders appear. Grazing electrons (for which $\lambda_{\perp} > a$) are reflected as before in the zeroth order of diffraction, i.e., with $k_{\parallel}^0 = \text{const}$.

The character of the electron reflection depends thus on the orientation of the physical boundary of the sample, on the topology of the equal surfaces of the metal, and on the symmetry that exists on the surface. We note also that an inclination of the surface of the metal away from the chosen symmetry plane gives rise on the system boundary to microscopic steps of atomic scale, each of which preserves the natural orientation and the translational symmetry of the chosen face of the crystal. For small disorientation angles ($\Delta\theta \approx 2$–$3°$) the number of steps on the boundary is small and the macroscopic surface reflects the electrons almost in the same way as in the ideal case.

Earlier investigations on tungsten and molybdenum single-crystal surfaces cleaned in vacuum have shown that the reflection of conduction electrons from the (110) faces of these metals is close enough to specular (the estimated specular-reflection coefficient p is 0.8–0.6). [3–5] The present paper is devoted to an investigation of cases when the symmetry on the surface has been artificially lowered. The long-range order on the boundary was destroyed by evaporating, on a perfect tungsten-crystal (110) face cooled to 4.2°, a structureless monoatomic tungsten film. The order could be restored by annealing the evaporated film at room temperature. Epitaxial copper films evaporated in ratios 1:1, 1:2, and 1:3 of the copper atoms to the tungsten surface atoms, fill-out (according to data obtained by the DME method[8]) the lattice of the tungsten crystal. The matching of the structures in the first atomic layer of the copper turns out to be good and decreases gradually with increasing number of the layer. For immediate copper concentrations, the film structure turns out to be imperfect to a considerable degree. This has enabled us to trace the periodic dependence of the specular-reflection coefficient on the concentration of the copper on the surface. Data on the character of the electron reflection were obtained in an investigation of

the skin effect and comparison with the theory of Peschanskiĭ and Azbel'.[7]

EXPERIMENTAL PROCEDURE

In general outline, the experimental procedure does not differ from that described earlier.[3-5] The measurements were made in a cryostat that made it possible to vary smoothly the temperature in the range from 4.2 to 300 °K accurate to 0.1°. The temperature in the working chamber of the cryostat was measured with a differential gold–chromel thermocouple and maintained constant with an electronic servomechanism. The investigated samples were cut from a high-purity ingot with a ratio $\rho(300 \text{ K})/\rho(4.2 \text{ K}) \sim 8 \cdot 10^4$, produced by crucibleless zone melting. Data on the impurity content in the investigated material are given in Table II of the paper of Shishkov et al.[8] (ingot No. 5). The electron mean free path at $T = 4.2$ °K is estimated at ~1 mm. The tungsten crystals were rectangular plates measuring $6 \times 2 \times 0.1$ mm and were oriented in the plane of the (110) face accurate to 15 minutes of angle. The defect-containing layer at the surface, resulting from the machining, was removed by electrochemical treatment in 5% lye solution. The subsequent surface finishing was under high-vacuum conditions (10^{-11} mm Hg) by the standard procedure used in SED research.[9] The construction of the glass vessel and the method of securing the sample were described in detail earlier.[8] The sources of the tungsten and copper atoms were installed in separate bulbs outside the cold part of the cryostat. The tungsten was evaporated from a single-crystal rod of high purity, mounted vertically in the experimental setup. Electron bombardment melts the lower end face of the rod, but the evaporable metal drop stays on the crystal because of the surface-tension forces. The copper source was a cylinder of 9 mm diameter, and the evaporator casing was made of molybdenum sheet metal; it had an opening of 1.5 mm diameter for the escape of the evaporated matter and was surrounded by a ring cathode. The copper was heated
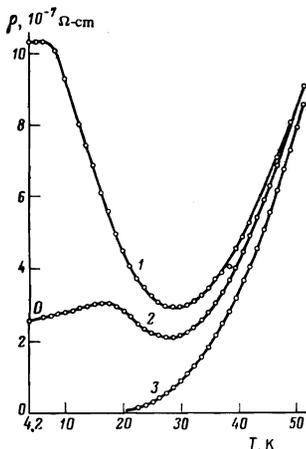
to the evaporation temperature by electron bombardment of the casing. In the course of the evacuation of the experimental setup, the sources were subjected to a rigorous conditioning, and the background pressure did not rise to more than 10^{-10} mm Hg when they were turned on. The atomic beams from the sources could be blocked by a shutter controlled by an external magnet.

The measurements were carried out in an electromagnet at a field intensity 8.9 kOe. The magnetic field was oriented in the plane of the plate and was perpendicular to the electric current flowing through the sample. The sensitivity of the null-method measuring circuit was 10^{-7} V.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 (curves 1 and 2) show the behavior of the resistance of a thin tungsten plate ($d = 0.1$ mm) in a constant 8.9-kOe magnetic field as a function of the temperature of the sample and the surface state. Curve 1 corresponds to the case when the plate surface was covered with an adsorbed film produced in the residual-gas atmosphere. Curve 2 was measured after "flash" cleaning the surface by short-durating high-temperature heating the crystal in vacuum. This plot is consistently reproduced for several hours after cleaning the surface. After long exposures, the crystal surface gradually adsorbs the residual gases, and the magnetoresistance of the plate returns to the initial one, i.e., to curve 1. Curve 3 of the same figure was obtained in the absence of a magnetic field. In this case the state of the surface plays no significant role (at least in the temperature region above 25 °K).

The plots shown in the figure can be interpreted in the following manner: It is known that in a strong magnetic field the conductivity of compensated metals varies in proportion to $(\omega_c \tau)^{-2}$, where ω_c is the cyclotron frequency and τ is the electron-momentum relaxation time. At low temperatures, and accordingly at large τ, the sample conductivity in a constant magnetic field ~10 kOe is smaller, according to estimates, by a factor ~10^4. In thin plates, the collisions of the electrons with the surface leads to a decrease of the effective time τ^*. In this case, the plate conductivity depends on the orientation of the magnetic field relative to the surface and on the character of the electron reflection. In a strong magnetic field ($\omega_c \tau \gg 1$) oriented parallel to the surface (and perpendicular to the electric field), allowance for the collisions with the boundary leads to the following expression for σ[7]:

FIG. 1. Resistivity ρ vs temperature T for a thin tungsten plate ($d = 0.1$ mm): 1 and 2—magnetic field $H = 8.9$ kOe directed parallel to the plate surface; 1—surface coated with monomolecular adsorbed film; 2—surface cleaned under high-vacuum conditions; 3—in the absence of a magnetic field.

$$\sigma = \sigma_0 \frac{\gamma}{q+\gamma} \frac{r}{d} + \sigma_0 \gamma^2. \tag{1}$$

Here σ_0 is the conductivity in the absence of a magnetic field; $\gamma = r/l$, where r is the Larmor radius; $q = (1 - p)$ is the phenomenological diffuseness coefficient. The first term in the right-hand side of (1) corresponds to the surface conductivity σ_{sur} due to that fraction of the carriers which interacts with the surface and moves along the surface in a relatively narrow layer of order
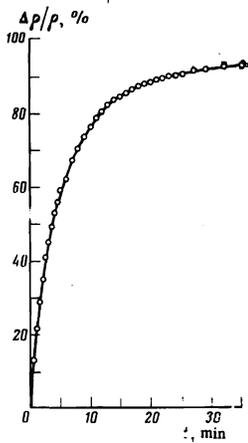
FIG. 2. Relative change of the magnetoresistance of a tungsten plate in a constant 8.9-kOe magnetic field as a function of the time of evaporation of the tungsten atoms on the surface of a crystal cooled to $4.2\,°K$.

r. In all cases (whether specular or diffuse reflection) their mobility turns out to be larger than in the interior of the crystal. With increasing number of specular reflections, σ_{sur} increases and the magnetoresistance of the crystal decreases. The saturation of curves 1 and 2 in the region of the lowest T indicates that $\sigma_{sur} > \sigma_0 \gamma^2$ and determines the conductivity of the plate in this temperature interval. A similar conclusion was drawn earlier[4,10] in a study of the magnetoresistance of thin tungsten plates as functions of their thickness at a constant temperature $4.2\,°K$. Thus, almost the entire current in the crystal flows in two narrow channels of thickness r located at the sample surface. As follows from (1), when the condition $q \gg \gamma$ is satisfied ($\gamma \sim 10^{-2}$ at $T = 4.2\,°K$ and $H \sim 10$ kOe), the expression for the surface conductivity σ_{sur} does not contain the quantity l: the number of jumps of the electron at the surface, and consequently the length of its drift in the conducting channel, is determined only by the probability of the specular reflection p and does not depend on the crystal temperature. In the limit $q = 1$ (diffusing surface) the drift length is equal to r and σ_{sur} does not depend on T. As seen from Fig. 1, for a "dirty" surface (and apparently $q \sim 1$) this law is satisfied in the region $T < 10\,°K$. At higher temperatures, the plate resistance decreases rapidly because of the increase of the relaxation time τ in the volume of the crystal. In the case of a clean surface, and therefore smaller q, the condition $q \gg \gamma$ may be violated in the intermediate temperature region, and in this case σ_{sur} is a function of T. Indeed, in the limit $q = 0$ (specular surface) the electron drift along the surface is limited only by l and consequently depends on T. Another possible cause of the increase of the magnetoresistance, observed in the interval up to $20\,°K$ (curve 2), is that q itself depends on T. It can be assumed that the thermodynamic-equilibrium Rayleigh sound wave propagating along the interface[11,12] disturbs quite strongly the shape of the crystal surface. The resultant dynamic disturbances of the boundary relief increase the diffuse background of the reflected electrons. We note, however, that to separate in experiment the contributions from the two considered mechanisms requires the use of much stronger magnetic fields.

Figure 2 shows a plot of the magnetoresistance of a thin tungsten plate against the evaporation time in a

constant stream of tungsten atoms on a cleaned crystal surface cooled to $4.2\,°K$. The initial state of the plate corresponds to the point O on curve 2 of Fig. 1. The magnetic field and the crystal temperature were maintained constant during the evaporation. The maximum atom concentration, corresponding to saturation of the $\Delta\rho/\rho$ curve, is $\sim 10^{15}$ cm^{-2}; it was estimated from the thickness of the film that settled on the walls of the glass vessel after several evaporation cycles. It is seen from the figure that a change in the state of the two crystal surfaces decreases the plate conductivity by almost one-half. This corresponds to a rather appreciable decrease, by one order of magnitude, of the current in one of the two conducting channels produced at the sample surfaces. The deposition of a very thin tungsten film, on the order of one atomic layer, which changes only the order of the arrangement of the surface-layer atoms, decreases significantly the coefficient p of the specular reflection of the electrons from the crystal boundary. Annealing the film at room temperature restores the magnetoresistance of the plate almost instantaneously to its initial value. If the experiment is repeated many times, the resistivity ρ of the plate remains practically unchanged, since its thickness increases insignificantly.

An automatically recorded plot of the magnetoresistance against time obtained in the course of continuous evaporation of copper on the same tungsten crystal, is shown by curve 1 of Fig. 3. These measurements were made at $4.2\,°K$. Plots 2 and 3 were also obtained at $4.2\,°K$ for cases when the copper films were annealed at 76 and $130\,°K$. These data were obtained in the following manner. In the course of the evaporation of the copper, the beam of atoms was covered at the instant when ρ of the plate reached, for example the value A on curve 1. After annealing the film for 10 minutes at $T = 76\,°K$, the ρ of the plate decreased to the value marked by the arrow in the figure. The next points on curve 2 were measured after first cleaning the surface completely, and then evaporating and annealing new batches of copper. The absolute concentration of the copper
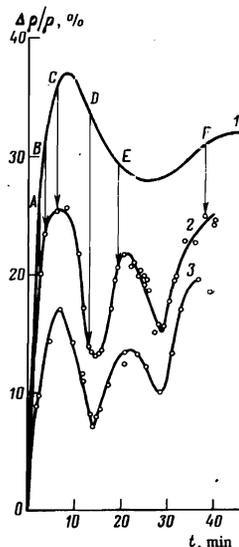
FIG. 3. Relative change of the magnetoresistance of a tungsten plate in a magnetic field $H = 8.9$ kOe as a function of the time of copper evaporation: 1—copper evaporated on crystal surface cooled to $4.2\,°K$; 2—copper film annealed at $T = 76\,°K$. At the points $A, B., C \ldots$ the beam of copper atoms was blocked with a shutter; 3—copper film annealed at $T = 130\,°K$.

was estimated from the change of the work function of the electrons leaving the surface. The minima on curves 2 and 3 appeared after the buildup of the first and second atomic layers of copper, and their depth, as seen from the figure, depended on the annealing temperature.

According to data obtained by the SED method,[6] the copper atoms evaporated at room temperature on the (110) face of the tungsten single crystal form in the first layer a regular lattice that duplicates the substrate structure. The next two layers also duplicate this structure, but the agreement between the substrate and the film decreases gradually. The minima on curves 2 and 3, which represent in final analysis the dependence of the specularity coefficient p on the copper concentration, is observed when the translational symmetry is restored on the surface. At large copper concentrations, the agreement vanishes gradually and the oscillations of p attenuate.

The character of the reflection of the conduction electrons from the surface of the metallic crystals thus depends on the type of the diffraction processes that are realized on the conductor boundary. If the translational symmetry on the crystal surface is preserved, the electron reflection can be close to specular.

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Translated by J. G. Adashko

Valence-change transitions in rare-earth compounds

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(Submitted March 5, 1976)
Zh. Eksp. Teor. Fiz. 71, 767–777 (August 1976)

The effect of exciton phenomena on the properties of localized impurity states and on the characteristics of electronic phase transitions with change of valence in rare-earth metals and compounds is considered. It it shown that Coulomb interaction between localized f-electrons and conduction electrons may broaden the narrow f-levels; this broadening depends (in contrast to the width of the virtual levels in the Anderson model) on the position of the E_0 level with respect to the Fermi energy; the width is maximal at $E_0 = \epsilon_F$. It is shown that if this effect is taken into account the f-level near ϵ_F may become stabilized and states with an intermediate valence may arise. In this case two consecutive phase transitions of the γ-α-α' type can occur in Ce under pressure. The influence of compressibility of the lattice is taken into account. The shapes of the phase diagrams of substances like Ce or SmS are discussed qualitatively.

PACS numbers: 71.55.Dp, 71.80.+j

1. INTRODUCTION

Rare-earth (RE) ions, both in metals and in compounds, are characterized usually by a definite occupation of the internal $4f$ shell with an integer number of f electrons; their state can be described by corresponding atomic quantum numbers (spin, orbital angular momentum, etc.). Direct overlap of the wave functions of the f electrons on different centers is usually small and depends little on their properties.

There are, however, a number of systems in which states of different valence are close in energy (for example, Sm^{2+} and Sm^{3+} in SmS). In these cases, transitions are possible between such states when the external conditions (pressure, temperature, composition) are changed, or, in other words, an f electron can go over into the conduction band (process of the type $Sm^{2+} \rightarrow Sm^{3+} + s$ electron). This phenomenon is assumed to be the cause of the experimentally observed, in a number of substances, electronic phase transitions, such as $\gamma - \alpha - \alpha'$ transitions in Ce[1] or dielectric–metal transitions in SmS, SmSe, SmTe,[2] TmTe,[3] EuO.[4] These phase transitions are usually not connected with a change in the lattice symmetry. They can be either first-order transitions (SmS, EuO), or continuous transitions (SmSe, SmTe); the corresponding phase-equilibrium line can terminate at the critical point ($\gamma - \alpha$ transition in Ce).