In superhigh-vacuum conditions (residual gas pressure less than $10^{-8}$ Pa), electroconductive dimensional phenomena, the Hall constant, and the absolute differential thermoemf of zirconium films are investigated. The experimental results are analyzed within the framework of current model concepts regarding volume, surface, and grain-boundary scattering of charge carriers (the Mayadas-Schatkes and Tel'e-Tosser-Pichard models). The charge-transfer parameters in zirconium are determined.

The investigation of kinetic phenomena in thin films yields information on charge transfer in the surface region of solids. It is known that, in thin films, volume scattering is accompanied by charge-carrier scattering at the external surfaces of the film [1] (the classical dimensional effect) and scattering by grain boundaries (the internal dimensional effect) [2]. Therefore, by changing the film thickness $d$ or the size $D$ of the crystallites in the film, the kinetic coefficients may be controlled, within certain limits.

In the present work, the dependence of the electrical resistivity $\rho$, the Hall constant $R$, and the absolute differential thermo-emf $S$ of polycrystalline zirconium films on the layer thickness is investigated. The method of preparing layers of titanium-group metals with reproducible structure and electrical properties was described in [3, 4]. Note that the experiment is conducted in sealed glass instruments at a pressure of the residual-gas active components of less than $10^{-8}$ Pa. On evacuating the instrument, special attention is paid to the degasification of the glass components of the instrument (they are heated at 450°C for at least 30-40 h) and to prolonged conditioning of the metal evaporation units at temperatures close to the evaporation temperature of zirconium (electronic heating is employed). The films are applied to polished-glass substrates cooled to 78 K and, after annealing at 360-370 K, the kinetic coefficients of the films are investigated directly in the instrument at $T = 300$ K. Electron-microscope and electron-diffraction studies show that the crystal lattice of the condensates is analogous to that of a massive metal, and the linear dimensions of the crystallites (12-15 nm) do not depend on the layer thickness.

The dependence of the kinetic coefficients of the films on the layer thickness $d$ is shown in Fig. 1. The real electron structure of the metal must be taken into account in calculating the charge-transfer parameters in zirconium films (free path $\lambda$, grain-boundary scattering coefficient of the charge carriers $r$, and transmission coefficient of the grain boundaries $t$). Zirconium is a transition metal with unfilled d states. Charge transfer in zirconium occurs over both electron and hole trajectories (as indicated by the sign of the Hall constant, $R > 0$). An analogous method of analyzing the experimental data was used, in particular, in [3].

It is assumed in this method that all forms of scattering influence the electron and hole components of the conduction independently, while the kinetic coefficients take the form [5].
Fig. 1. Dimensional dependence of the kinetic coefficients of the films: 1) S; 2) \( \rho \); 3) \( R \).

\[
\sigma = \frac{1}{p} = \sigma^+ + \sigma^-; \\
R = \frac{1}{Ne} \left( \frac{n^+ \sigma^+ - n^- \sigma^-}{n^+ \sigma^+ + n^- \sigma^-} \right); \\
S = \frac{\pi^2 \hbar^2 T}{3eE_F} \frac{\sigma^+ - \sigma^-}{\sigma}
\]

Here \( N \) is the atomic concentration of the material; \( n^+ \) and \( n^- \) are the mean numbers of electron and hole trajectories per atom; \( \sigma^+ \) and \( \sigma^- \) are the electrical resistivities of the sample on account of electron and hole trajectories; \( k \) is the Boltzmann constant; \( E_F \) is the Fermi energy of the material; \( T \) is the absolute temperature; \( e \) is the elementary charge.

It follows from [6, 7] that the Hall constant of massive zirconium samples \( R_0 = 0.227 \cdot 10^{-10} \text{ m}^3/\text{C}, n^- = 2, n^+ = 0.003 \), and the ratio of contributions of the electron and hole conductivities is \( \sigma^-/\sigma^+ = 22.3 \). The results of calculating the dimensional dependences of \( \sigma^- \) and \( \sigma^+ \) for the films on the basis of the experimental data using Eqs. (1) and (2) are shown in Fig. 2. The form of the curves of \( \sigma^- = \sigma^-(d) \) and \( \sigma^+ = \sigma^+(d) \) may be explained using the model concepts of [1, 2]. According to [1], a product of the type \( [1/\sigma(d)]d = \rho(d)d \) must be a linear function of the layer thickness, and the slope of the straight line is \( \rho_\infty \), the resistivity of an infinitely thick plate (as \( d \to \infty \)). The free path length of current carriers \( \lambda \) in an infinitely thick film may be determined from the intercept \( d' \) corresponding to this straight line on the abscissa

\[
d' = \frac{3}{8} (1 - p) \cdot \lambda.
\]

where \( p \) characterizes the degree of specularity of the surface scattering. Infinitely crystalline zirconium films, \( p = (0.0-0.1) \) [4]. According to the data for \( \sigma^- = \sigma^-(d) \) and \( \sigma^+ = \sigma^+(d) \), it follows that \( \rho^- = 180 \cdot 10^8 \text{ \Omega \cdot m}, \rho^+ = 2700 \cdot 10^8 \text{ \Omega \cdot m}, \) and \( \lambda^- = 24 \text{ nm}, \lambda^+ = 5 \text{ nm} \). Comparison of \( \rho^- \) and \( \rho^+ \) with the corresponding parameters of a massive metal [6] shows that \( \rho^-/\rho_\infty = 0.236 \) and \( \rho^+/\rho_\infty = 0.35 \).

The contribution of grain-boundary scattering is calculated using the model concepts proposed in [2, 8]. In [2], it was shown for films that are monolithic over the thickness that \( \rho_0/\rho_\infty = f(\alpha) [4] \), and the free path length of current carriers in a massive material

\[
\lambda_0 = \lambda_0 / f(\alpha).
\]

Here

\[
f(\alpha) = \left(1 - \frac{3 \alpha}{2}\right) + 3 \alpha^2 - 3 \alpha^3 \ln \left(1 + \frac{1}{\alpha}\right).
\]

\( \alpha = \lambda_0 r/D(1 - r) \); \( D \) is the mean diameter of the crystallite; \( r \) is the grain-boundary scattering coefficient. The transmission coefficient of current carriers through the grain boundaries \( t \) may be determined using the relation [9]