Numerous experiments (see, e.g., the reviews 1 and 2) have established that at helium temperature the resistivity of a transition metal is quadratic in the temperature. This fact is interpreted as a rule as a manifestation of electron-electron collisions with a frequency calculated theoretically (Refs. 3–6) to be proportional to \( T^2 \). However, the electron-electron collisions can lead to a noticeable contribution to the resistivity only when conditions of electron-electron umklapp processes, as a result of which the total wave vector of the interacting electrons is changed by an amount equal to the reciprocal-lattice vector, or else in the case of collisions between oppositely charged carriers (electrons and holes in a compensated metal).\(^7\) The rather large quadratic contribution to the resistivity of transition metals is frequently attributed to collisions between conduction electrons having substantially different Fermi velocities.\(^4\) This explanation, however, cannot be used for all the transition metals, and at any rate not for tungsten. The point is that the recent theoretical and experimental investigations of the Fermi surface of this metal, have shown that the velocities of the different electron groups do not differ enough to account for the experimentally observed values of this contribution. For example, according to results on the radio-frequency size effect\(^6\) the Fermi velocities of the carriers of the electron "jack" \( \Gamma' \), of the hole "octahedron" \( H \), and of the hole "ellipsoids" \( N \) differ by not more than a factor of two. The question was therefore raised\(^7\) of the nature of the quadratic-in-temperature contribution to the resistivity of transition metals, particularly tungsten.

Moreover, the low-temperature behavior of the resistivity of tungsten, which is usually described at \( T \lesssim 10-15 \) K by the expression\(^8\)

\[
\rho(T) = \rho(0) + \alpha T^2 + \beta T^3.
\]

(1)

calls for further experimental study for the following reasons.

First, there is an extraordinarily large scatter in the values of the coefficient \( \alpha \); according to the data of Refs. 10–18, \( \alpha \) ranges from 0.4 to \( 3.5 \times 10^{-12} \) \( \Omega \cdot \text{cm} \cdot \text{K}^{-2} \). So large a scatter exceeds the measurement errors by more than one order of magnitude, and cannot be explained.

Second, in the preceding measurements of \( \rho(T) \) of tungsten, the crystallographic orientation of the faces of the samples was not monitored. Under the condition \( l > d \) (\( l \) is the average transport mean free path of the electrons and \( d \) is the sample thickness), which is inevitably realized in pure single-crystal tungsten samples at liquid-helium temperature, the interaction of the electrons with the sample surface can greatly influence the temperature dependence of the resistivity.

Third, most measurements of \( \rho(T) \) of tungsten\(^9,10,11,16\) were made in a narrow temperature interval at \( T \lesssim 7 \) K. This pertains also to measurements of the frequency of the collisions of the electrons by the methods of radio-frequency\(^7\) and magnetoacoustic\(^14\) size effects, in which the upper temperature limit did not exceed \( -15 \) K. Yet it is of considerable interest to know whether \( \alpha \) remains constant when the temperature is raised.

In view of the existing experimental situation, we have carried out precision measurements, in the wide temperature interval \( 2-40 \) K, of the temperature dependences of the resistivity of single-crystal samples of tungsten with different crystallographic orientations of their faces. The ratio \( \rho_{\text{diff}}/\rho_{\text{int}} \) of the initial bulk crystals was 155 000 and 140 000. In each pure bulky crystals, the transport mean free path of the conduction electrons at 4.2 K is about 5 mm [estimates based on formulas (3) and (4)], and the temperature-dependent part of the resistivity becomes larger than the impurity-scattering background starting with \(-6 \) K, while at \( T=20.4 \) K it exceeds the background by 50 times. It can therefore be assumed that this temperature interval corresponds to the "pure limit."
SAMPLES AND MEASUREMENT PROCEDURE

The samples were cut by the electric-spark method and subsequently ground and electrically polished in an NaOH solution. They were bars of quadratic cross section and plates 40 mm long. The dislocation density in the samples prepared by this method, measured by the "etch-pit" method, did not exceed 2 \times 10^6 cm\(^{-2}\).

The sample thickness ranged from 3 to 0.15 mm. The long axes of the samples were oriented along one of the principal crystallographic directions, (100), (110), or (111), and the planes of the samples coincided with crystallographic planes of the type (100), (110), or (112). The orientation of the samples was monitored by x-ray diffraction, and the sample dimensions were measured with an M-1 microscope. The characteristic of some of the samples are listed in the table.

The resistivity was measured by a potentiometer method: the sensitivity of the apparatus was 10\(^{-7}\) V. For the measurements of \(\rho(T)\) we used a cryostat in which the temperature was set and maintained automatically with accuracy not worse than 0.01 K. Below 15 K, the temperature was measured with a TSG-2 germanium thermometer accurate to 0.05 K, and above 15 K it was measured with a TSPN-2A platinum thermometer accurate to 0.01 K. The measurement errors are indicated on the figures.

MEASUREMENT RESULTS AND THEIR DISCUSSION

Figure 1 shows the temperature dependences of the resistivities of two tungsten samples that differ only in size, in the interval 2-40 K. We call attention to the following experimental facts.

First, the \(\rho(T)\) dependence cannot be described in the entire temperature interval from 2 to 40 K by expression (11), even though the condition \(T<0.1\alpha\), is satisfied (the Debye temperature of tungsten is \(\Theta_D = 379\) K).

Second, there exist two temperature intervals, 2-12 and 20-40 K, in which the coefficients \(a\) and \(b\) in expression (1) for \(\rho(T)\) differ substantially. The boundary between these temperature intervals depends on the sample thickness and corresponds to the condition \(l/d \\sim 0.1\).

Third, in the "high-temperature" interval 20-40 K, where \(l<d\), the coefficient \(a'\) is close to zero and does not exceed 0.05 \(\times 10^{-10} \Omega \cdot \text{cm} \cdot K^3\) within the limits of the measurement accuracy. In the "low-temperature" interval 2-12 K, where \(l=d\), the values of \(a'\) exceed the values of \(a\) by more than one order of magnitude and increase with decreasing sample thickness.

These experimental facts give grounds for assuming that the quadratic-in-temperature contribution to the resistivity of tungsten is due to scattering of the conduction electrons by the surface of the samples, i. e., to the size effect. If this assumption is correct, then the contribution of the size effect to the resistivity of the tungsten at \(T=4.2\) K should be substantially different for samples having identical dimensions and purities, but different crystallographic orientations of the faces. This statement is based on the results of recently published experiments, in which the methods of electron focusing\(^{19}\), of the static skin effect\(^{20}\), and of Sondheimer oscillations\(^{21}\) have established that an electrically polished\(^{20}\) single-crystal tungsten surface reflects the conduction electrons with a larger degree of specularity (the specularity coefficient is \(q=0.6-0.8\)) than the (100) plane \((q=0.3)\).

To assess the influence of the character of electron reflection from the sample surface on the resistivity of tungsten at \(T=4.2\) K, and to estimate quantitatively the contribution of the size effect to its temperature-de-

### TABLE I

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current direction</th>
<th>Orientation of faces</th>
<th>Sample dimensions, mm</th>
<th>(\alpha) in (\times 10^{-10} \Omega \cdot \text{cm} \cdot K^3)</th>
<th>(\beta) in (\times 10^{-10} \Omega \cdot \text{cm} \cdot K^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115 km</td>
<td>(100)</td>
<td>(100)</td>
<td>4.25 (\pm 0.05)</td>
<td>12.0 (\pm 0.0)</td>
<td>(5.58 \pm 0.05)</td>
</tr>
<tr>
<td>115 km</td>
<td>(100)</td>
<td>(100)</td>
<td>3.3 (\pm 0.05)</td>
<td>30.7 (\pm 0.0)</td>
<td>(3.1 \pm 0.5)</td>
</tr>
<tr>
<td>115 km</td>
<td>(100)</td>
<td>(100)</td>
<td>3.1 (\pm 0.05)</td>
<td>24.2 (\pm 0.0)</td>
<td>(2.1 \pm 0.1)</td>
</tr>
<tr>
<td>115 km</td>
<td>(100)</td>
<td>(100)</td>
<td>5.5 (\pm 0.05)</td>
<td>24.2 (\pm 0.0)</td>
<td>(2.1 \pm 0.1)</td>
</tr>
<tr>
<td>115 km</td>
<td>(100)</td>
<td>(100)</td>
<td>6.0 (\pm 0.05)</td>
<td>24.2 (\pm 0.0)</td>
<td>(2.1 \pm 0.1)</td>
</tr>
<tr>
<td>115 km</td>
<td>(100)</td>
<td>(100)</td>
<td>5.5 (\pm 0.05)</td>
<td>24.2 (\pm 0.0)</td>
<td>(2.1 \pm 0.1)</td>
</tr>
</tbody>
</table>

*Temperatures interval 27-40 K.
pendence, we have performed two groups of experiments.

1. Dependence of the resistivity of single-crystal tungsten samples with different crystallographic faces on the transverse dimensions at $T = 4.2$ K.

Figure 2a shows plots of the tungsten resistivity $\rho_{\text{W}}$ against $1/d$, measured at $T = 4.2$ K on samples of quadratic cross section in the thickness interval 0.6–2.6 mm and at various orientations of the current. Assuming that the character of the electron reflection from the sample surface does not depend on the angle of encounter of the conduction electrons with the surface, the size effect for samples of this form can be described by the relations:

$$\rho(d) = \rho(0) + (1 + 0.75(1 - q^*)/d). \quad \text{Eq. (2)}$$

$$\rho(d) = \rho(0) \frac{1 + 0.9}{1 + 0.9/d}. \quad \text{Eq. (3)}$$

where $q^*$ is the Fuchs parameter corresponding to the relative number of electrons specularly reflected from the surface. It is seen that for samples having only faces of the (100) type the contribution of the size effect is substantially larger than for samples with {110} and {100} faces, as well as with {110} and {112}, i.e., containing a pair of planes with orientation {110}. The appreciable slope of line 1 (Fig. 2a) compared with lines 2 and 3 could be qualitatively attributed to the fact that the specular reflection of the conduction electrons from that electrically polished single-crystal tungsten surface that corresponds to the (100) plane is much lower than for {110}.

However, according to calculation, the resistivity dependence, we have performed two groups of experiments.

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However, according to calculation, even in metals with cubic symmetry, the slope of the plots of $\rho_{\text{W}}(1/d)$, can be affected also by the orientation of the current relative to the crystal if $l > d$. To exclude this factor, we measured the $\rho_{\text{W}}(1/d)$ dependence for samples with different crystallographic faceting, but at the same orientation of the measuring current relative to the crystal. It is seen that the slope of $\rho_{\text{W}}(1/d)$ is determined by the crystallographic type of the plane corresponding to the faces of the sample, and amounts to $15.3 \times 10^{-14}$ and $6.9 \times 10^{-14}$ $\Omega \cdot cm^2$ for samples with faces {100} and {110}, respectively. If it is assumed that the parameters $q$ and $q^*$ are close in value, no.1 for samples with {100} faces in accordance with Refs. 20–22, then an estimate made according to (3) for samples with {110} faces in the thickness interval $0.5-2.6$ mm yields $q^* = 0.5$, in satisfactory agreement with the results of Refs. 20–22.

According to the estimates, the average transport mean free path of the electrons in a tungsten crystal with $p_{\text{W}}/\rho_{\text{W}} = 115 000$ at $T = 4.2$ K is $4.8$ mm, while in a crystal with $p_{\text{W}}/\rho_{\text{W}} = 140 000$, corresponding to line 2 of Fig. 2b, the path is $5.8$ mm. Thus, in the experiments performed on the $p_{\text{W}}(1/d)$ dependence, the investigated sample-thickness interval corresponds to a change in the values of $1/d$ approximately from 2 to 10.

To obtain additional evidence that the differences between the slopes of the $p_{\text{W}}(1/d)$ plots is due precisely to the different character of the electron reflection, two plates, with the appropriate planes, were cut from a sample measuring $2.64 \times 2.60$ mm, and with {110} and {110} faces (this sample, with "mixed" character of the reflection, corresponds to the first point on line 2 of Fig. 2a). The ratio of the plate thickness to their width was $0.5$. Thus, these plates had identical dimensions, the same impurity concentration, and a common crystallographic direction of the long axis, i.e., direction of the measuring current), and differed only in the relative areas of the {100} and {110} faces. The transverse dimensions of the plates were subsequently decreased successively by electric polishing.

The measurements results are shown in Fig. 2c,11. It is seen that the increase of the area of the "diffusely" scattering surface {100} enhances the size effect, and an increase of the area of the "specular" reflecting surface {110} weakens it.

Thus, these experiments have shown that the contribution of the size effect to the resistivity of single-crystal tungsten samples at $T = 4.2$ K depends substantially on the crystallographic type of their faceting and is determined by the character of the reflection of the conduction electrons. This nontrivial fact must be taken into account if a correct estimate is to be made of the
electric purity of the tungsten by the method of the residual resistivity.

2. Influence of the character of the reflection of the conduction electrons from the sample surface on the temperature dependence of the resistivity

The results of the experiments described above give grounds for expecting the contribution from the size effect to the temperature dependence of the resistivity of tungsten, and consequently to the value of the coefficient \(a\) in the low-temperature interval, to depend substantially on the crystallographic type of the plane (surface) of the crystal. We have therefore measured \(\rho(T)\) for two thin plates. The samples of each pair had identical dimensions and purity, and differed only in the crystallographic orientation of the surface: \([100]\) or \([110]\). The value of \(\rho(T)\) of each pair measured simultaneously under identical conditions. As seen from Fig. 3, the values of \(\rho_{100}\) for plates with diffusely reflecting plane \([100]\) exceed substantially the values of \(\rho_{110}\) for plates with \([110]\) plane. The difference between these coefficients is unaffected by changes of the orientation of the measuring current and becomes stronger with decreasing plate thickness (also see the table).

Figure 4 shows the directly measured temperature dependence of the difference between the resistivities of the plates of thickness 0.15 mm \(\Delta(T) = (\rho - \rho_{110})_{100} - (\rho - \rho_{110})_{110}\). The quantity \(\Delta(T)\) does not include the residual resistivity or the contributions due to direct electron-phonon and electron-electron collisions, or to scattering by the vibrating impurity ions. It is a measure of the resistivity temperature dependence due only to scattering of the conduction electrons by the metal surface. As seen from Fig. 4, \(\Delta(T)\) is a function of the temperature dependence of \(\Delta(T)\) or the contributions due to direct electron-phonon and electron-electron collisions, or to scattering by the vibrating impurity ions. It is a measure of the resistivity temperature dependence due only to scattering of the conduction electrons by the metal surface. As seen from Fig. 4, \(\Delta(T)\) is a function of the difference between the resistivities of the plates with planes \([100]\) and \([110]\), \(\Delta(T)\) to the first two mechanisms.

Another possible cause of the observed \(\Delta(T)\) dependence may be connected with the Olsen mechanism.28 It is possible that this effect takes place in tungsten.29 However, direct proof of a manifestation of \(\eta'(\alpha)\) in the resistivity of tungsten single crystals would be the observation of a decrease in the slope of the plot \(\rho(1/d)\) with decreasing sample size, as was observed for antimony whiskers.25 We note that the results of our experiments, which were performed under conditions \(2 < l/d < 10\), cannot be interpreted solely within the framework of the calculations of Refs. 26 and 27, inasmuch as the latter are valid only for extremely thin samples, when \(l >> d\) and \(d/l < T/\theta_J\). In the experiments, on the other hand, the contribution \(\Delta(T)\) is observed in a wide interval \(2-12\) K for the inverse inequality \(d/(l/T) < T/\theta_J\), all the way to \(l(T)-d\).

Another possible cause of the observed \(\Delta(T)\) dependence may be connected with the Olsen mechanism.28 The point is that in very thin samples the electron-phonon-collision at low temperatures can lead to a subsequent scattering of the electron by the sample surface. According to a calculation performed for \(\eta' = \theta_J\), make a resistivity contribution proportional to \(T^2\).
The condition \( T < 2 \text{K} \) is close to \( T = T_0 \) which follows from (4).

A major shortcoming of the calculation of Ref. 30, however, is that it takes no account of the \( \phi(T) \) dependence.

The experimental data on the dependence of the quadratic-in-temperature contribution to the resistivity of tungsten on sample thickness, which was obtained by us earlier, have shown that the coefficient \( \sigma' \), measured in the interval 2-12 K under the condition \( I \gg d \), is proportional to \( T^{1/2} \) (see Fig. 5 of Ref. 31). It turned out there that \( \sigma' \) decreases with decreasing ratio \( I/d \) and does not exceed 0.06 x \( 10^{-12} \) \( \Omega\cdot\text{cm} \cdot \text{K}^2 \) determined in the interval 20-40 K (Fig. 1 and the table), where the influence of the size effect can be neglected by virtue of the temperature resistivity of transition metals. One must subtract the contribution due to the surface scattering, as well as to the electron-phonon interference between the electron-phonon and electron-surface scattering.

Thus, with tungsten as the example, we have shown that the quadratic-in-temperature dependence of the low-temperature resistivity of transition metals one must bear in mind the possible substantial increase (by one order of magnitude or more) of the coefficient \( \sigma' \) on account of the interference between the electron-phonon and electron-surface scattering.

The authors thank Yu. P. Gaidukov and V. F. Gantmakher for helpful remarks and for interest in the work.

\[ \rho_{\text{eff}}(T) = (8n/3)(\alpha'(T))^{1/2}(\rho_{\text{Cu}}^{0.5})^{1/2}T^{1/2}, \]

where \( \rho_{\text{eff}} \) is the resistivity due to the normal electron-phonon collisions. The experimentally obtained dependence of the electron-surface scattering on the temperature \( \phi(T) \) is close to \( T^{3/4} \) which follows from (4).

\( \phi(T) \) is close to \( T^{5/2} \).

The plates with (111) were the same as used to investigate the size effect at \( T = 4.2 \text{K} \) (Fig. 2).

Inasmuch as in the electric polishing process the ratio of the plate thickness to their width is invariably changed (in our case from 1/3 to 1/6), these results cannot be used to estimate the parameter \( \phi' \).

\[ \rho_{\text{Cu}}^{0.5} = \text{constant}, \]

\[ \rho_{\text{eff}}(T) = (8n/3)(\alpha'(T))^{1/2}(\rho_{\text{Cu}}^{0.5})^{1/2}T^{1/2}, \]

Translated by J. G. Adashko