Electronic properties of whiskers

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Usp. Fiz. Nauk **142**, 571–597 (April 1984)

When the mean-free path length of conduction electrons in a metal l^∞ is comparable to the thickness of the specimen d, various kinds of size effects appear. To study these effects, under the cleanest conditions, filamentary crystals—whiskers—are used. At low temperatures conditions under which $l^\infty \gg d$ are easily achieved in whiskers. In this case the interaction of electrons with the surface is determining, and this markedly changes the electronic properties characteristic for the usual massive ($d \gg l^\infty$) specimens. In this review the results of the experimental study of the effect of dimensions on the electrical resistance of whiskers, permitting the determination of the degree of specularity of the reflection of electrons from the surface, are examined. In a magnetic field under the condition that $l^\infty \gg d,r$ the theory predicted new phenomena: a dc skin-effect confined to a thin (of the order of the Larmor radius r) surface layer of the specimen, a change in the quantum effects for $r > d$, as well as other effects. Experiments on whiskers in which these phenomena are observed are described in this review. Experiments in which the high (close to the theoretical limit) strength of whiskers is used to investigate electronic 2.5-order transitions are also described.

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1. INTRODUCTION

The samples used in physical investigations must, in most cases, be specially prepared under artificial conditions, and it is only in rare exceptions that nature itself provides experimenters with objects that are ideally suitable for this purpose. An excellent example of this are filamentary and plate-like single crystals, which are collectively referred to as whiskers.

Although the existence of whiskers has been known for a long time, it is only in the last two or three decades that these unusual formations have attracted the attention of investigators. Interest in whiskers was elicited by the fact that they have a number of unique properties which the usual massive single crystals do not have. This raised hopes for extensive use of whiskers in measuring instruments and in technical applications. In many cases these hopes were justified.

Most of the work that has been performed involves the investigation of the physics of nucleation and growth of whiskers, which is of great scientific value both for the physics of crystal growth in itself and for practical applications For example, spontaneous growth of whiskers on thin layers of metallic coatings leads to damage in different electronic systems. The practical value of measures which would eliminate these undesirable phenomena is obvious.

The morphology of whiskers is very diverse. Included are long filaments and ribbons, thin platelets, tubular and spiral-shaped crystals, cones and wedges, etc. For this reason the term whisker refers, in general, to a single crystal, growing freely under both natural and artifical conditions, with a large disproportion of linear dimensions. For example, the length of the crystal can exceed its thickness by a thousand-fold or, in the case of a platelet, the thickness of the crystal can be smaller by a similar factor than the two other dimensions of the plate. In most cases whiskers have faceting; the facets can be parallel to the crystallographic planes of high symmetry.

In the definition of the term "whisker" the words "growing freely" mean "not in a enclosure" or "not on a substrate." This is important because it allows one to distinguish whiskers from microconductors and films, although with respect to many physical properties the latter are analo-

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gous to whiskers. For example, whiskers as well as microconductors and films can be used to study static size effects.

Whiskers of many compounds as well as pure chemical elements are now known. Almost all metals have been grown in the form of whiskers. The thicknesses of whiskers fall in the range 10^{-6}–10^{-2} cm. The length can attain several centimeters.

Some materials crystallize only in the form of whiskers with a filamentary form. These include various fibrous minerals, such as asbestos. Such crystallization is related to the strong anisotropy of the molecular structure. At the same time, the growth of whiskers of metals and other elements whose crystals have high symmetry is unexpected and puzzling.

Several models have been proposed for the growth of whiskers. The most widely used model at present is the so-called VLC model (the name is formed by the first letters of the words indicating the successive phases through which the molecules of the material pass during the growth of the crystals: vapor–liquid–crystal). Although the physical nature of the initial phase of the nucleation of a whisker and of the growth process itself and of its termination are not yet completely understood, the practical problems involved in growing whiskers of different materials have been successfully solved in most cases. Whiskers can grow in a vacuum or a gas and both from and in a solution. The material for growth can enter either directly onto the surface of the growing crystal from the surrounding medium or from the base on a substrate. Growth occurs from both the base and the apex of the whisker.

A large part of the monographs by Berezhkova[1] and Givargizov[2] is concerned with the problems of growing whiskers. At the same time the physical properties of whiskers, especially whiskers of metals, are examined only cursorily in these works.

The purpose of this paper is to demonstrate by a number of examples the remarkable opportunity that whiskers present for investigations of the electronic properties of metals.

What makes whiskers so attractive as an object of physical investigations? The answer to this question lies primarily in the truly unique properties of whiskers: their small dimensions and high chemical purity, the perfection of their surface and bulk structure, and their high strength, which is close to the theoretical limit. It is precisely these properties that have led to the discovery of new phenomena and that have made it possible to obtain results which cannot be obtained using the usual massive single crystals.

2. SIZE EFFECT IN THE RESISTIVITY OF METALS

A) Restriction of the mean-free path of conduction electrons by the dimensions of the sample

For the unbounded medium, when scattering by the faces of the sample can be neglected, the resistivity ρ^∞ is a characteristic of the metal and does not depend on the shape and dimensions of the sample. The situation can change considerably, however, if the mean-free path l^∞, determined by the scattering of conduction electrons in the bulk by phonons, lattice defects, and impurities, becomes comparable to or even greater than the transverse dimensions of the specimen d. In this case the boundaries of the sample will restrict the mean-free path and, in the limiting case when $l^\infty \gg d$, the effective mean-free path $l^d \to d$. This situation arises in very thin specimens of pure metals at low temperatures (the corresponding resistivity is denoted below by ρ^d). It was therefore necessary to clarify the effect of dimensions on kinetic phenomena in metals, which elicited a large amount of both theoretical and experimental work on size effects.

The simplest size effect is the dependence of the resistivity of the sample on the thickness. It is understandable that for the conditions under which the size effect is manifested the concept of "resistivity" loses its original meaning, since it no longer reflects the properties of the material and depends on the geometry and dimensions of the sample.

The effect of dimensions on the resistance was discovered at the end of the last century and already in 1901 J. J. Thompson gave the correct explanation of this effect: the additional resistance appears due to the scattering of electrons by the surface of the sample. A theoretical analysis of the size effect is contained, for example, in the books by Ziman[3] and Green.[4]

An important point in the theory of the size effect is, naturally, the boundary condition for the electron distribution function. Until recently, it was written in the form proposed by Fuchs[5,1)]:

$$f_1(r_s,\ \mathbf{p}) = P f_1(r_s,\ \hat{\mathbf{p}}), \tag{1}$$

where f_l is the nonequilibrium correction to the distribution function, r_s is the coordinate of the particle on the surface, $\hat{\mathbf{p}}$ is the momentum of the incident particle, and $\mathbf{p}$ is the momentum of the reflected particle. Here, the parameter P describes the average reflectivity of the surface of the sample.[2)] The magnitude of P lies in the range $0 \leqslant P \leqslant 1$. The reflection from the surface is considered to be completely specular for $P = 1$ and completely diffuse for $P = 0$. An intermediate value of P indicates partially specular reflection and to some extent characterizes the surface, if samples with identical geometry and thickness are being compared. Fuchs's parameter P does not contain any definite information on the structure and physical state of the surface. The relation between Fuchs's parameter P and the probability of specular reflection in a number of cases is examined in Ref. 4.

Experimental results are usually analyzed based on a comparison with Fuchs's theoretical calculations[5] for plates and Dingle's calculations[7] for wires.

In the limiting cases of thin or thick samples, we have the following relations between the resistance ρ^d and the thickness of the specimen d:

$$\left.\begin{aligned} \rho^d &= \rho^\infty + \frac{4}{3}\frac{\rho^\infty l^\infty}{d}(1-P), & l^\infty &\ll d, \\ \rho^d &= \rho^\infty + \frac{\rho^\infty l^\infty}{d}\left(\frac{1-P}{1+P}\right), & l^\infty &\gg d, \end{aligned}\right\} \text{wires}, \tag{2}$$

1) A detailed theoretical examination of the present status of the problem of boundary conditions for the distribution function is given in Ref. 6. In particular, the concepts of specular and diffuse reflection of electrons from the surface of a metal are formulated and the cases for applicability of conditions of the type (1) are discussed.

2) Formally, the quantity p can be viewed as the fraction of electrons specularly reflected from the surface.

$$\left.\begin{aligned}\rho^d&=\rho^\infty+\frac{3}{8}\,\frac{\rho^\infty l^\infty}{d}\,(1-P), & l^\infty&\ll d,\\ \rho^d&=\rho^\infty+\frac{4}{3}\,\frac{\rho^\infty l^\infty}{d}\left(\ln\frac{l^\infty}{d}\right)^{-1}\frac{(1-P)}{(1+P)}, & l^\infty&\gg d.\end{aligned}\right\}\ \text{plates}. \tag{3}$$

(If $l^\infty \gg d$ and $1-P \gg d/l^\infty$, the quantity ρ^∞, of course, can be neglected. However, for the following analysis it is important to retain this quantity.) For cubic crystals $\rho^\infty l^\infty = 12(\pi\hbar)^3/e^2 s_f$, where s_F is the area of the Fermi surface[8]; for anisotropic cases it is necessary to introduce a factor of the order of one, which takes into account the orientation of the sample.[9]

At room temperature the mean-free path l^∞ is determined by the electron-phonon interaction and is of the order of 10^{-5} cm. For a long time this retarded progress in the study of size effects. The situation changed considerably when low temperatures became accessible and superpure materials appeared. At temperatures obtained with the help of liquid helium ($T \simeq 4$ K) the main contribution to scattering comes from the interaction of electrons with lattice defects and impurities. For this reason, in very pure metals the mean free path of electrons can reach magnitudes of the order of 1.1 cm. The preparation, in this case, of specimens with different thicknesses, comparable to l^∞, with identical quality no longer presents great technical difficulties, and this permits obtaining reliable and reproducible results.

At the outset of the study of the size effect specular reflection from the surface ($P \neq 0$) appeared to be implausible. For this reason, the experimental dependence $\rho^d(d)$ was used to determine the magnitude of the product $\rho^\infty l^\infty$, which permitted evaluating the dimensions of the Fermi surface. The inverse problem was also formulated: using model calculations of the Fermi surface, the theoretical and experimental dependences $\rho^d(d)$ were compared. It is interesting to note that most of the early experimental work supported completely diffuse reflection, i.e., the experimental results were described best by $P=0$ (see, for example, Ref. 3, p. 419). However, under conditions characteristic for these investigations, when $l^\infty \simeq d$, and with the use of the simplest model considerations of the Fermi surface of a metal, the conclusion that $P=0$ had to be viewed not as an experimental fact but rather as a plausible conclusion, corresponding to the contemporary views of the nature of the interaction of electrons with a real metallic surface.

b) Size effect in the resistance of whiskers

Beginning approximately in 1960, under the pressure of experimental facts, the view concerning the possibility of specular reflection of electrons from the surface began to change gradually. The position has now changed so radically that the possibility of complete diffuse scattering is viewed as an unlikely phenomenon. Experimental investigations of the effect of size on the resistivity of whiskers played a large role in this amazing transformation in the views of the nature of reflection. Whiskers permitted performing measurements under conditions when $l^\infty \gg d$. This condition is achieved, on the one hand, by the fact that modern experimental technique permits electrical mounting of samples with thicknesses up to 10^{-5} cm.[10,11,12] On the other hand, in the most widely used methods for growing metallic whiskers (spontaneous growth and growth from the gas phase) the chemical purity and especially the structural perfection of whiskers can be better than in the starting metals used for growing purposes. This is confirmed by experiments in which quantum oscillations of the resistance in a magnetic field (Shubnikov–de Haas effect) are investigated. At the lowest temperatures the amplitude of the oscillations depends on the purity and physical perfection of the specimens. This dependence is characcterized by the Dingle temperature T_D.[13] The higher the purity and perfection of the metal sample, the lower is its T_D temperature and the higher is the amplitude of quantum oscillations. Figure 1, taken from Ref. 14, shows a trace of the Shubnikov–de Haas effect for two samples of antimony. One specimen is a platelet whisker and the other is a massive sample, obtained from the starting material used to grow the whiskers. The specimens have the same crystallographic orientation and the measurements were performed under identical conditions. It is evident that the amplitude of the oscillations is higher in the case of the whisker. Analysis of the experimental curves shows that $T_D \simeq 3.5$ K for the massive sample and $\simeq 1$ K for the whiskers, i.e., the whiskers are "pure" and l^∞ must therefore be higher for them.

An idea of the magnitude of l^∞ for whiskers can also be obtained by determining the magnitude of ρ^∞ from measurements of the dependence $\rho^d(d)$ (see expressions (2) and (3)). Extrapolation of this dependence to $d^{-1}=0$ gives the magnitude of ρ^∞. The accuracy of this procedure is usually not high, but it is still possible to assert that in order of magnitude ρ^∞ and, therefore, l^∞ for the starting material and for the whiskers coincide (Fig. 2).

Thus if pure materials are used for growth, then at low temperatures l^∞ in whiskers can reach values of 10^{-1}–1 cm and it is possible to obtain ratios l^∞/d of the order of 10^3–10^4.

Under the conditions of a strong size effect ($l^\infty \gg d$), practically all electrons collide with the surface. In this case the electrons approaching the surface under small angles have a higher probability of being scattered specularly. The relative contribution of such electrons to the conductivity of the sample increases with increasing ratio l^∞/d, which causes the Fuchs parameter P to increase. The difference from the case of completely diffuse reflection becomes so

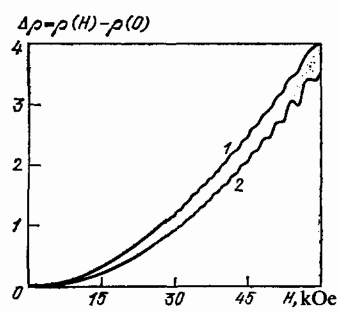

FIG. 1. Dependence of the increment to the resistance of antimony on the magnetic field parallel to the trigonal axis of the crystal.[14] The resistance is given in arbitrary units; $T=4.2$ K. Curve 1-massive sample of thickness 2 mm; curve 2-whisker of thickness 11 and width 100 μm.

large that the conclusion of partially specular reflection becomes unavoidable.

The magnitude of P is usually estimated by comparing two series of measurements. A massive sample whose thickness is decreased by successive etching is used in one series and whiskers are used in the other. Assuming that for the etched samples $P = 0$, using Eqs. (2) and (3) it is possible to estimate the magnitude of P for whiskers. The results of such experiments are presented in Figs. 2 and 3.

For "good" metals the values of the parameter P for whiskers with a thickness of the order of 10^{-4} cm fall in the range 0.5–0.8. Even higher values should be expected for semimetals such as bismuth and antimony.

The high value of the parameter P for whiskers is related not only to the satisfaction of the condition for a strong size effect but also to the high degree of perfection of the surfaces bounding the whisker. Moreover, these surfaces, as a rule, coincide with the crystallographic planes of high symmetry, for which specular reflection is most probable.[4,17] If such a surface is artificially defected (for example, by etching), then the resistance is observed to increase, indicating that the "diffuseness" of the surface has increased (see Fig. 2).

3. TEMPERATURE DEPENDENCE OF THE RESISTANCE OF WHISKERS

a) Deviation from Matthiessen's rule

A serious argument in favor of the existence of specular reflection of electrons from the surface was obtained in experiments performed on whiskers for the purpose of studying the deviation of the resistance of thin samples from Matthiessen's rule. According to Matthiessen's empirical rule, the resistance of a metal with a small amount of impurity can be written as a sum of two terms:

$$\rho^{\infty} = \rho_0 + \rho_i(T). \tag{4}$$

The first term ρ_0—the residual resistance—does not depend on the temperature and is related to scattering of electrons by impurities and lattice defects. The second term $\rho_i(T)$ is called the ideal resistance. It depends on the temperature and is related to scattering by phonons. Thus the residual resistance characterizes the quality of the sample, whereas the ideal resistance is a characteristic of the metal itself. Matthiessen's rule can be given a theoretical justification, if it is assumed that the scattering by impurities, defects, and phonons are independent of one another.

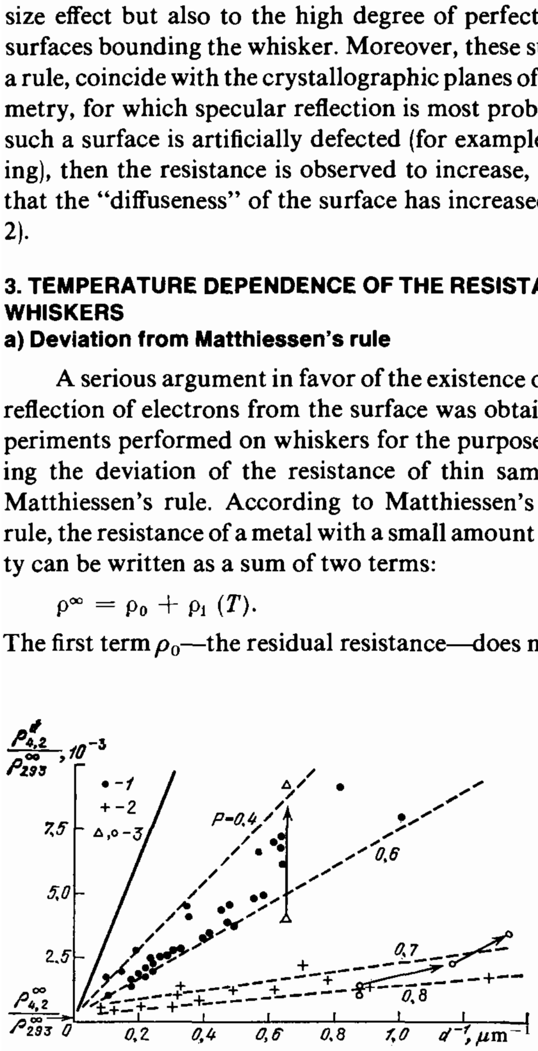

FIG. 2. Effect of size on the resistance of zinc whiskers.[12] 1-Filamentary samples, 2-plates. Zinc, for which $\rho^{\infty}_{4.2}/\rho^{\infty}_{293} \approx 10^{-4}$ was used to grow the samples. The symbols 3 refer to filamentary and platelike whiskers from Ref. 11. The arrows mark the results of subsequent chemical etching of the samples. The continuous line indicates extrapolation to small thicknesses of the resutls obtained in Ref. 15 on the determination of the dependence $\rho(d^{-1})$ of massive samples. Their thickness was varied by chemical etching. Assuming that for these samples the specularity parameter $P = 0$, the dashed lines in the figure show the behavior of the resistance according to Eqs. (2) and (3) in the text for values of P indicated by the numbers: 0.4 and 0.6 for filamentary whiskers and 0.7 and 0.8 for plate-like whiskers.

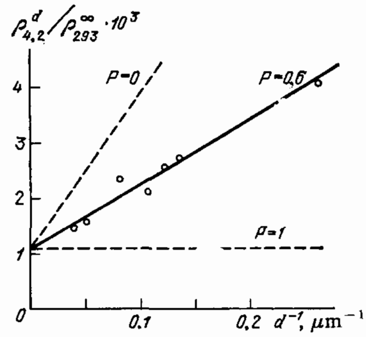

FIG. 3. Effect of size on the resistance of filamentary copper whiskers.[16] The circles show the experimental points; the straight line shows the calculation for different values of P with $\rho^{\infty} l^{\infty} = 0.65\cdot 10^{-11}$ $\Omega\cdot$cm^2.

Since a collision with the surface can be viewed as an efficient and independent source of scattering of electrons, the following question arises. Is Matthiessen's rule valid in the case of the size effect, i.e., is it possible to write

$$\rho^d(T) = \rho_0 + \rho_s + \rho_i(T), \quad \rho_i^d(T) = \rho_i^{\infty}(T),$$

where ρ_s—the additional "surface" resistance—does not depend on the temperature?

With completely diffuse scattering the resistance of samples with a circular and rectangular cross section in limiting cases can be written in the form (see expression (2)).

$$\rho^d = \rho^{\infty} + A\frac{\rho^{\infty} l^{\infty}}{d} = \rho_0^{\infty} + \rho_i^{\infty}(T) + \rho_s,$$

where A is a number of the order of 1. For "good" metals with a high concentration of current carriers the product $\rho^{\infty} l^{\infty}$ and, therefore, ρ_s do not depend on temperature, so that Matthiessen's rule should be satisfied. This conclusion is also valid for plates in the case $d \gg l^{\infty}$. At the same time, for $d \ll l^{\infty}$ the logarithmic term in the denominator of expression (3) leads to a small deviation from Matthiessen's rule. In the intermediate region $l^{\infty} \approx d$, according to calculations using the Fuchs–Dingle model,[5,7] a small deviation should also be observed from Matthiessen's rule.

A deviation from Matthiessen's rule was observed in wires and films of different metals (see Ref. 18, p. 114). The general conclusion that can be drawn from these experiments is that the observed deviation is much larger than follows from the theory.

To explain this disagreement a mechanism that takes into account scattering by small angles was invoked. Expressions (2) and (3) were obtained under the assumption that the contribution to the resistance from scattering of electrons by phonons does not depend on the angle between the direction of motion of the electrons and the surface of the sample.

However, this condition may not be satisfied at low temperatures, which was first pointed out by Olsen.[19] According to Olsen, if $1 \gg T/\theta \gg d/l^\infty$ (θ is the Debye temperature) the collision of an electron moving toward the surface at a sharp angle with a phonon leads to its collision with the surface. As a result the momentum of the electron changes by an amount comparable to the momentum itself. Olsen's mechanism must increase the efficiency of electron-phonon collisions in a thin sample at low temperatures and should lead to a significant increase of the temperature dependent part of its resistance as compared with the massive specimen. Quantitative calculations using this mechanism were performed by Blatt and Satz[20] and also by Azbel' and Gurzhi.[21] Below, we shall consider the results obtained in Ref. 21, because in this paper the results were obtained for the most general case–for both wires and plates.

In a thin specimen ($d \ll l^\infty$), at low temperatures, the effective frequency[3)] of collisions of electrons, gliding along the surface, with phonons is higher than in the bulk: $\nu^d_{ep} \gg \nu^\infty_{ep}$. In the massive sample $\nu^\infty_{ep} \propto (T/\theta)^3 (T/\theta)^2$), where the factor $(T/\theta)^3$ takes into account the number of phonons and the factor $(T/\theta)^2$ is due to the low efficiency of electron-phonon collisions (scattering by a small angle of the order of T/θ). In a thin sample, for gliding electrons (the angle between the direction of motion and the surface is less than d/l^∞), a collision with a low-frequency phonon is effective because it leads to the collision of electrons with the surface, where diffuse scattering is assumed. For this reason, for gliding electrons $\nu^d_{ep} \propto (T/\theta)^3$. Since in thin specimens current is primarily transported by gliding electrons, the electron-phonon mean-free path is $l^d_{ep} \propto (T/\theta)^3$ and, correspondingly, the temperature-dependent part of the resistance $\rho^d_i(T) \propto (T/\theta)^3$. This must be valid if

$$T/\theta \gg \frac{d}{l^\infty_{ei}}, \quad \left(\frac{d}{l^\infty_{ep}}\right)^{1/3}, \tag{5}$$

where l^∞_{ei} is the mean-free path due to impurities.

For an arbitrary relation between d/l^∞ and T/θ the resistance of a thin specimen with completely diffuse scattering is given by the following expressions:

for plates

$$\rho^d \approx \rho^\infty + \frac{\rho^\infty l^\infty}{d}\left[\ln\left(1+\frac{1}{x_0}\right)\right]^{-1}, \tag{6}$$

for wires

$$\rho^d \approx \rho^\infty + \frac{\rho^\infty l^\infty}{d}(1+\delta), \tag{7}$$

where

$$\delta = \frac{d}{l_{ei}}\ln\frac{1}{x_0} + \frac{1}{2}\frac{d}{l^\infty_{ep}}\left(\frac{\theta}{T}\right)^2 \ln\left[1+\left(\frac{T}{\theta}\right)^2\frac{1}{x_0^2}\right],$$

$$x_0 = d\left(\frac{1}{l_{ei}}+\frac{1}{l^\infty_{ep}}\right) + \frac{d}{l^\infty_{ep}}\left[\left(\frac{T}{\theta}\right)^2 + \left(\frac{d}{l^\infty_{ep}}\right)^{2/3}\right]^{-1}.$$

Analysis of these equations shows that in the general case the residual resistance for thin samples is attained at much lower temperatures than in massive samples. In addition, at the lowest temperatures ($T/\theta < d/l^\infty_{ii}$) $\rho^d(T) \propto T^5$, since a collision with a phonon no longer leads to a collision with the surface and under the condition (5) $\rho^d(T) \propto T^3$.

In order for it to make sense to compare the size-induced deviations from Matthiessens' rule to the theoretical predictions, the measurements should be performed on homogeneous samples with a small amount of impurities and defects. In this case, reliable results can be obtained only for a strong size effect $l^\infty \gg d$.

The temperature behavior of the resistance of zinc and cadmium whiskers was studied in Refs. 22–24. Measurements were peformed primarily for filamentary whiskers with micron thickness with $l^\infty \approx 0.1$ cm at $T = 4.2$ K. Considerable deviations were observed from Matthiessen's rule. At low temperatures ($T < 10$ K) the ideal resistance $\rho^d_i(T)$ exceeded many-fold $\rho^\infty_i(T)$ for massive samples. The results of the measurements are presented in Fig. 4. However, the theory[21] was not confirmed. First of all, in spite of the fact that condition (5) was satisfied with much room to spare, differences were not observed in the degree of dependence of the resistance on the temperature: massive samples and thin whiskers obeyed approximately the same law. Thus, in zinc whiskers with $d \approx 1\ \mu$m in the temperature range 4–12 K $\rho^d_i(T) \propto T^{4.4\pm0.2}$, and for the massive sample $\rho^\infty_i(T) \propto T^{4.6\pm0.2}$. A small difference was observed in cadmium: $T^{4.9\pm0.2}$ and $T^{5.0\pm0.3}$. Second, although the observed deviations from Matthiessen's rule were significant, they still were one to two orders of magnitude smaller than the theory predicted.[21] The predicted dependence of the temperature part of the resistance on the thickness of thin samples was also not confirmed. According to Ref. 21, $\rho^d_i(T) \propto \ln(d^{-1})$, whereas experiment gave the dependence $\rho^d(T) \propto d^{-1}$.

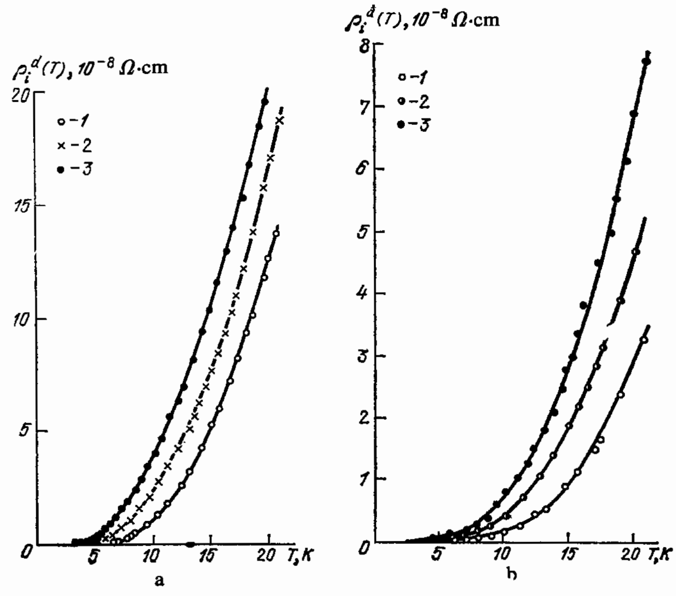

FIG. 4. Dependence of the ideal resistance of massive samples and whiskers on temperature. a) Samples of cadmium[23] (experimental points: 1-massive sample, $d = 1.2$ mm, 2-filamentary whisker, $d = 3.2\ \mu$m; 3-same, $d = 1.45\ \mu$m); b) samples of Zinc[22] (experimental points: 1-massive sample, $d = 1.2$ mm; 2-filamentary whisker, $d = 2.4\ \mu$m, 3-same, $d = 1\ \mu$m).

3)That is, the frequency of collisions which lead to a change in the momentum of an electron by an amount comparable to this momentum.

Such a large qualitative and quantitative disagreement between theory and experiment required a reexamination of the basic assumptions of the theory. In this connection, it was proposed in Ref. 22 that Olsen's mechanism is absent in thin whiskers. For Olsen's mechanism it is significant that the reflection from the surface is diffuse for any angle of incidence of the electron on the surface. It is precisely the diffuseness of the reflection even for "gliding" electrons that must lead, under the condition (5), to the elimination of the factor $(T/\theta)^2$ in the expression for $\rho_i^\infty(T)$. However, by the time that the work in Refs. 22, 23, and 24 was performed it was already clearly established that in metals reflection for electrons incident on the surface at small angles is specular.[25] Since the "gliding" electrons make the main contribution to the conductivity of thin samples, it would appear that it is precisely the specularity that decreases the effectiveness of Olsen's mechanism. It is evident from expressions (2) and (3), for example, that with completely specular reflection ($P=1$) the size effect is entirely absent. However, this has not been confirmed experimentally. It has been established that the etching-induced increase of the "diffuseness" of the surface of whiskers, decreases the difference between the ideal resistances of whiskers and massive samples.[24] In order to give a constant description of all characteristics of the temperature dependence of the resistance of whiskers, it was proposed that the experimental results be described with the help of expressions (2) and (3), making the assumption that Fuchs's parameter depends on the temperature: $P = P(T)$. Formally, this can be done in any case, since the parameter P was essentially introduced, as an adjustable parameter in order to obtain the best agreement between theory and experiment. Without delving into the nature of the dependence $P(T)$, it is still natural to assume that as the temperature increases the magnitude of P decreases from the maximum value at low temperatures $P_0 \leqslant 1$ to zero at high temperatures, when $l^\infty \ll d$. Correspondingly, the diffuseness parameter, defined as $Q = 1 - P$, increases from $Q_0 = 1 - P_0$ to $Q = 1$. Then, from expression (2) for thin wires it follows that the deviation from Matthiessen's rule is related to the dependence $P(T)$, it is maximum for $P_0 = 1$ and it is absent for $P_0 = 0$. In the most general case, the following inequalities should be satisfied:

$$-\frac{1}{4}\frac{\rho^\infty l^\infty}{d} \leqslant \Delta\rho_i^d(T) \leqslant \frac{\rho^\infty l^\infty}{d}, \qquad (8)$$

where $\Delta\rho_i^d = \rho_i^d(T) - \rho_i^\infty(T)$.

By virtue of the inequalities (8), in studying Matthiessen's rule for thin specimens it is in principle impossible to neglect the difference between ρ^d and ρ^∞ even at high temperatures. It is usually[4)] assumed in this case that $\rho^d \equiv \rho^\infty$, which, naturally, leads to a distortion of the results at high temperatures, since the effect sought should not exceed the difference $\rho^d - \rho^\infty$. The maximum value of the difference $\Delta\rho_i^d(T)$ will be attained at some temperature $T_{\rm dif}$ above which $P=0$. At high temperatures ($T > T_{\rm dif}$ and $l^\infty \ll d$) the difference between the ideal resistances is a constant:

$$\Delta\rho_i^d(T)_{\max} = \frac{\rho^\infty l^\infty}{d}\left(\frac{3}{4} - \frac{1-P_0}{1+P_0}\right). \qquad (9)$$

Thus Matthiessen's rule will be satisfied only at high temperatures.

These considerations formed the basis for the analysis of the experimental dependences of the resistance of filamentary zinc and cadmium whiskers, obtained over a wide range of temperatures from liquid helium to room temperatures.[24] The resistance ρ^d (293 K) was calculated from expression (2) under the assumption that total diffuse reflection occurs at room temperature. The results are shown in Figs. 5 and 6. It is evident that the difference $\Delta\rho_i^d(T)$ decreases, if the initial specularity of the surface of the whiskers is decreased by etching (the initial value $P_0 \approx 0.5$ and after etching $P_0 \approx 0.3$). The quantity $\Delta\rho_i^d(T)$ increases with temperature and saturates at comparatively low temperatures; in addition $T_{\rm dif} \approx 20$ K for cadmium and $T_{\rm dif} \approx 40$ K for zinc. At saturation the quantity $\Delta\rho_i^d(T)$ coincides with the estimate (9). All this permits extracting the dependences $P(T)$ and $Q(T)$ from the experimental data. Figure 7 shows the dependences of the diffuseness parameter Q and of the normalized specularity parameter P/P_0 on temperature. The universal nature of the dependence P/P_0 on the reduced temperature $T/T_{\rm dif}$ is interesting.

One possible reason for the dependence $P(T)$ could be related to the thermal "roughness" of the surface of the crystal, arising due to surface phonons. The interaction of an electron with surface phonons leads to a dependence of the probability W of specular reflection on the temperature. Green[4] examined such an interaction and found a relation between Fuchs's parameter P and the probability of scattering by surface phonons.

Although the question of the efficiency of thermal

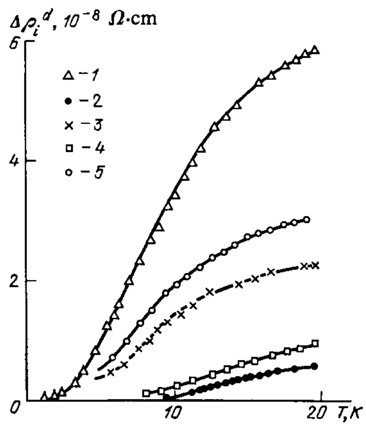

FIG. 5. Dependence of the difference of the ideal resistances of thin and massive samples on temperature $\Delta\rho_i^d(T) = \rho_i^d(T) - \rho_i^\infty(T)$.[24] Experimental points: 1-filamentary cadmium whiskers, $d = 1.45\ \mu$m; 2-filamentary cadmium whisker, $d \approx 2.6\ \mu$m; 3-same whisker after etching, $d \approx 2.6\ \mu$m; 4-filamentary zinc whisker, $d \approx 3.3\ \mu$m; 5-same whisker after etching, $d \approx 3.3\ \mu$m.

[4)] The quantity $\rho^d(T)$ is found as follows: $\rho^d(T) = (R(T)/R_{293})\rho_{293}^\infty$, where R is the experimentally measured resistance of a thin sample. At low temperatures, when $\rho^d \gg \rho^\infty$, this does not lead to a significant error. At high temperatures this method is in principle not applicable, since $\rho^d(T)$ must be known with high accuracy. This accuracy is not achieved by direct determination of ρ^d from the resistance and the dimensions of the sample. For this reason, to find $\rho(293)$ expression (2), in which the tabulated value of ρ^∞ and $P=0$ are used, can be employed.

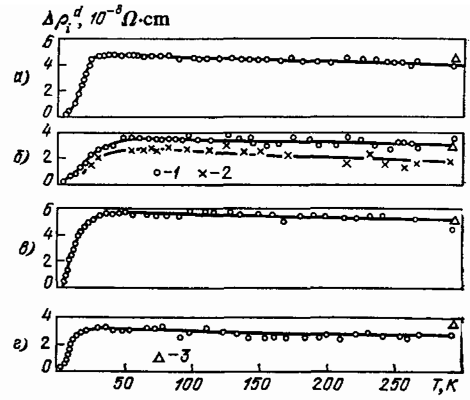

FIG. 6. Dependence of the difference of the ideal resistances of thin and massive samples on temperature.[24] a) Filamentary zinc whisker, $d = 1.3$ μm; b) same, $d = 2$ μm, 1-before etching, 2-after etching; c) filamentary cadmium whisker, $d = 1.6$ μm; d) same, $d = 2.2$ μm, 3-values of $\Delta\rho^d(T)$ calculated from Eq. (9) in the text.

"roughness" has not yet been completely clarified, a more realistic approach to the explanation of the reasons for the temperature dependence of p was nevertheless found by examining the question of the contribution of gliding electrons to the conductivity with a change of the ratio d/l^∞. Green introduced into the analysis the dependence of the probability of specular reflection on the angle of approach of the electron to the surface $W(\alpha)$ and he showed that the parameter P must depend considerably on the ratio d/l^∞ with $P \to 1$ as $d/l^\infty \to 0$.

Thus the dependence $P(T)$ arises even in the case when the probability of specular reflection does not depend on the temperature. This is related to the fact that, as already noted above, electrons incident on the surface at small angles $\alpha < d/l^\infty$ make an increasingly larger contribution to the total conductivity of a thin sample as its thickness decreases or its mean-free path increases. Since the probability of specular reflection increases with the angle α, the "specularity" of the surface, defined in terms of the parameter P, increases. Thus the question of the temperature dependence of Fuchs's parameter is closely related to the question of the dependence of the probability of specular reflection on the angle of approach of the electron to the surface.

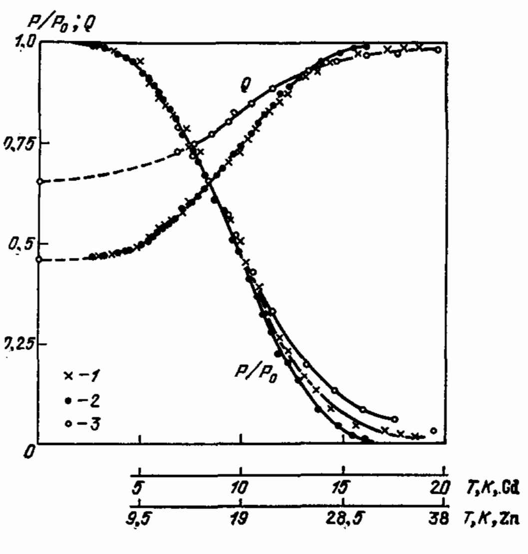

FIG. 7. Dependence of the specularity parameter P and diffuseness parameter $Q = 1 - P$ on the temperature for filamentary cadmium and zinc whiskers.[24] $P_0 = P(0,K)$. Experimental points: 1-cadmium, $d = 1.45$ μm; 2-zinc, $d = 1.3$ μm; 3-cadmium, $d = 2.6$ μm, after chemical etching.

b) Angular dependence of the probability of specular reflection

This important question in the physics of surface phenomena was raised a long time ago, but experimental methods for resolving it appeared only recently. Several methods are known: the study of the oscillations of the impedance in weak magnetic fields and the study of the cyclotron resonance on reflected electrons,[25,27] the method of transverse focusing of electrons in a magnetic field,[28,29] the method of comparing the temperature behavior of the resistance of thin and massive samples.[30] The latter reduces to the following.

Let the interaction of conduction electrons with the surface of the sample be described by the probability of specular reflection, depending only on the angle of incidence, $W = W(\alpha)$. We shall find a relation between the conductivity of a thin plate and that of a massive sample. The dispersion law of the metal is assumed to be isotropic and the temperature $T \ll \theta$.

If volume collisions are absent, then the mean-free path of an electron, hitting the surface of the plate at an angle α, is restricted by collisions with the surface. We shall examine only small angles α, for which the reflection is nearly specular. In moving from one surface to another the electron traverses a distance equal to d/α in the direction of the current. After colliding with the surface the electron will traverse the same distance with probability $W^2(\alpha)$, etc. Then, the distance the electron will traverse without scattering will equal

$$l^d = l(\alpha) + \frac{d}{\alpha} W(\alpha) + \frac{d}{\alpha} W^2(\alpha) + \ldots = \frac{d}{\alpha[1 - W(\alpha)]}. \quad (10)$$

Volume collisions limit l^d by a magnitude of the order of l^∞, so that it may be assumed that l^d is of the order of $l(\alpha)$ if $l(\alpha)$ is less than l^∞, and $l^d \sim l^\infty$ if $l(\alpha) > l^\infty$. We shall denote by α^* the angle at which $l(\alpha^*)$ equals l^∞. For an arbitrary angle we can write in a general form

$$l^d(\alpha) = \left[\frac{1}{l^\infty} + \frac{1}{l(\alpha)}\right]^{-1}.$$

The fraction of the electrons which are reflected in a narrow range of angles α, $\alpha + \Delta\alpha$ and acquiring an energy from the field E along the path $l^d(\alpha)$ is proportional to $\Delta(\alpha)$. For this reason, the total current I and, therefore, the average electrical conductivity $\sigma^d = (I/E)d$ are proportional to

$$\int_0^{\pi/2} l^d(\alpha)\, d\alpha.$$

Electrons incident on the surface in the range of angles $\alpha < \alpha^*$, for which $l^d(\alpha) \approx l^\infty$, make the main contribution to the conductivity of a thin plate. This range is limited by the condition $l^d(\alpha^*) = l^\infty$.

From expression (10) we find

$$\alpha^*[1 - W(\alpha^*)] = \frac{d}{l^\infty}. \quad (11)$$

On the other hand, we can write for the ratio of the conductivities

$$\frac{\sigma^d}{\sigma^\infty}=\frac{\rho^\infty}{\rho^d}=\frac{1}{l^\infty}\int\limits_0^{\alpha^*} l^d(\alpha)\,\mathrm{d}\alpha \approx \alpha^*. \tag{12}$$

Substituting (10) into (11), we obtain

$$W(\alpha^*)=1-\frac{\rho^d d}{\rho^\infty l^\infty}=1-\frac{\rho^d d}{\mathrm{const}}. \tag{13}$$

Expressions (12) and (13) determine the dependence $W(\alpha)$ being sought.

To find it from the experimental data it is necessary to measure the dependence of the resistances $\rho^d(T)$ and $\rho^\infty(T)$ and to know the quantity $\rho^\infty l^\infty$. This procedure for finding $W(\alpha)$ was used in Ref. 31, where the temperature behavior of the resistance of plate-like antimony whiskers was measured. The final result of the anlaysis of experimental curves, leading to the dependence $W(\alpha)$, is shown in Fig. 8. It is evident that for small angles, for which the theoretical calculations are valid, the dependence $W(\alpha)$ is linear.

The problem of the dependence $W(\alpha)$ was discussed theoretically by Green[4] and Andreev.[17] Andreev showed that reflection from a surface of high symmetry, which has defects with a size of the order of interatomic distances, leads to the dependence

$$W(\alpha)=1-2ap_F\alpha, \quad \alpha\ll 1, \tag{14}$$

where p_F is the Fermi momentum and a is the characteristic size of the surface roughness. Applying expression (14) to the results presented in Fig. 8 we find that for the antimony whiskers investigated $a\sim 10^{-8}$ cm, which confirms the view that the surface of whiskers is a very perfect formation.

4. RESISTANCE OF WHISKERS IN A MAGNETIC FIELD

a) Size effect in the magnetoresistance

The size effect becomes significantly more complicated in a magnetic field because together with the length l^∞ another quantity with the dimensions of a length appears: the radius r of the orbit of an electron in a magnetic field. Different ratios between d, l^∞, and r as well as the different geometry of samples and mutual orientation of the measuring current and of the magnetic field **H** give rise to the most diverse size effects. But they are always manifested against the background of a complicated behavior of the volume magnetoresistance, which depends strongly on the ratio of the number of electrons and holes and the geometry of the Fermi surface of the metal.

Size effects are much more distinct in the simplest behavior of the volume magnetoresistance (weak dependence on the magnetic field). This has permitted, on the one hand, observing them reliably experimentally and, on the other hand, obtaining a satisfactory theoretical interpretation of the observed phenomena. The most general characteristic feature of size effects in this case is the decrease in the role of surface scattering of electrons, beginnning with fields for which the radius r becomes less than the thickness of the sample d. In fields for which $r\ll d$ size effects disappear and the dependence of the resistance of a thin specimen on the magnetic field coincides with the dependence for a massive sample: $\rho^d(H)\to\rho^\infty(H)$. A condensed review of this subject can be found in Ref. 32.

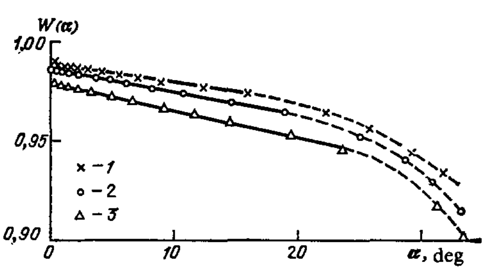

FIG. 8. Dependence of the probability of specular reflection on the angle of arrival at the surface for platelike antimony whiskers of different thickness.[31] 1-$d=0.25\,\mu$m; 2-$d=0.35\,\mu$m; 3-$d=0.75\,\mu$m. The surfaces of the plates are parallel to the basal plane of the crystal.

The general theory of galvanomagnetic phenomena in metallic samples with finite thickness taking into account the nature of the scattering of electrons by the surface, the ratio of the numbers of electrons and holes, and the shape of the samples for weak $(r>d)$ and strong $(r<d)$ magnetic fields[5)] was constructed by Azbel' and Peschanskiĭ.[33,34] The main idea of those investigations which determines a new approach to the examination of size effects in the magnetoresistance, consists of the fact that in strong fields electrons colliding with the surface have a higher mobility than electrons in the bulk of the sample. In a field parallel to the surface of the sample and perpendicular to the current, the effective mean-free path of electrons colliding with the surface equals r in the case of diffuse reflection and l^∞ in the case of specular reflection. This greatly increases the conductivity of the surface layer σ^s with thickness r:

$$\sigma^s_{\mathrm{dif}}(H)=\sigma^\infty(0)\frac{r}{l^\infty}, \quad \sigma^d_{\mathrm{spec}}(H)=\sigma^\infty(0).$$

Instead of $\sigma^\infty(H)=\sigma^\infty(O)(r/l^\infty)^2$. In many cases the current in the sample may, as a result, be concentrated almost entirely in this layer. This phenomenon is called the "static skin effect" (dc skin effect). The skin effect exists only when the resistance of massive samples increases quadratically with the field $\rho^\infty(H)\propto H^2$, which is characteristic for metals with an equal number of holes and electrons (compensated metals) and metals with open Fermi surfaces.[35]

The static skin effect must be manifested most distinctly in samples in the form of plates. In this case the nature of the reflection from the surface depends considerably on the form of the dependence $\rho^d(H)$. Indeed, the total conductivity of the specimen is

$$\sigma^d(H)=\sigma^s(H)\cdot\frac{2r}{d}+\sigma^\infty(H), \quad \sigma^\infty(H)=\sigma^\infty(0)\left(\frac{r}{l^\infty}\right)^2.$$

If the field is parallel to the surface of the sample, then even in the case of purely diffuse reflection the surface contribution to the conductivity is greater (with respect to l^∞/d) than that of the volume contribution and the latter can be neglected. Then, in the two limiting cases, the magnetoresistance in strong magnetic fields $r\ll d$ is given by the expression

$$\rho^d_\parallel(H)=\begin{cases}\rho^\infty(0)\dfrac{d}{2r}\propto H, & \text{specular reflection},\\[2mm] \rho^\infty(0)\dfrac{dl^\infty}{2r^2}\propto H^2, & \text{diffuse reflection}.\end{cases} \tag{15}$$

[5)]Everywhere below it is assumed that the condition $r\ll l^\infty$ is always satisfied (the condition of a strong magnetic field for volume galvanomagnetic phenomena).

For and arbitrary form of the reflection of electrons from the surface of the plate, the dependence of the resistance of the sample on the magnetic field under the same conditions is given by the expression

$$\rho_{\parallel}(H)=\rho^{\infty}(0)\frac{d}{2r}\,\frac{q+(r/l^{\infty})}{r/l^{\infty}}. \qquad (16)$$

In this expression the parameter q is the analog of Fuchs's diffuseness parameter. It is obtained by averaging the probability of specular reflection $W(\alpha)$ over the angle α.

For the case of a strong magnetic field, perpendicular to the surface of the plate, the nature of the interaction of electrons with the surface does not play an important role. The form of the dependence is the same as for a massive sample with an effective mean-free path of the order of d:

$$\rho_{\perp}^{d}(H)\approx\rho^{\infty}(0)\frac{l^{\infty}}{d}\left(\frac{d}{r}\right)^{2}\propto r^{2}d\propto H^{2}. \qquad (17)$$

For weak fields $r>d$, according to the theory, the nature of the reflection of electrons from the surface does not affect the conductivity of the sample, and the resistivity of the thin plate has the form:

$$\rho^{d}(H)\propto\rho^{\infty}(0)\frac{l^{\infty}}{d}\left(\ln\frac{r}{d}\right)^{-1}, \qquad \mathbf{H}\perp\mathbf{I}. \qquad (18)$$

In the region $d/2<r<d$ the resistance decreases as $2r\to d$ according to a linear law

$$\rho_{\parallel}^{d}(H)\propto\rho^{\infty}(0)\left[1+\beta\frac{l^{\infty}}{d}\left(1-\frac{d}{2r}\right)\right], \quad \beta\approx 1. \qquad (19)$$

In a longitudinal magnetic field $H\parallel I$, for $r>d$, the theory predicts a small increase in the resistance by an amount of the order of $\rho^{d}(0)$ for $r\approx\sqrt{(l^{\infty}d)}$, and then a decrease. In a strong longitudinal field $r\ll d$, due to the spiraling of the trajectories of the electrons, the surface does not affect the resistance and $\rho^{d}(H)\to\rho^{\infty}(0)$.

All cases of the behavior of the resistance of thin plates in a magnetic field examined above are shown in Fig. 9.

Whiskers are ideal objects for checking the results of the theory of the size effect and of the static skin effect in a magnetic field. They have the favorable relation $d\ll l^{\infty}$, which permits neglecting the volume part of the resistance. They have flat faceting, which is most favorable for the appearance of the static skin effect. The surfaces of whiskers are perfect and have a high reflectivity.

Since, cadmium, and antimony whiskers were investigated in Refs. 36, 37, and 38. In these metals the number of electrons equals the number of holes. A distinct size effect was observed: for specimens with the same orientation but

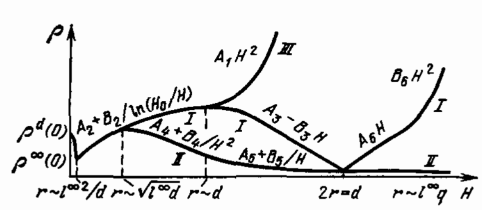

FIG. 9. Theoretical dependences of the resistance on the magnetic field for a thin plate with equal concentration of electrons and holes. I-The field H is perpendicular to the current and parallel to the plane of the plate; II-H is parallel to the current; III-H is perpendicular to the current and inclined or perpendicular to the plane of the plate.

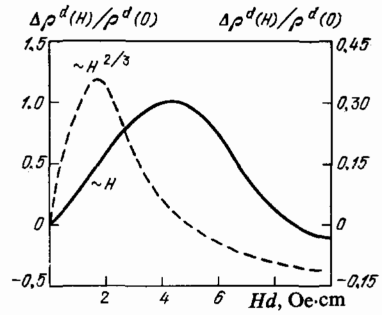

FIG. 10. Generalized experimental curves for the dependence of the resistance of zinc whiskers on the magnetic field parallel to the measuring current.[36] $T=4.2$ K. $\Delta\rho^{d}(H)=\rho^{d}(H)-\rho^{d}(O)$. The dashed curve is for the field and current parallel to the $\langle 1\bar{2}13\rangle$ axis (scale on the left); the continuous curve is for field and current parallel to the $\langle 1\bar{2}10\rangle$ axis (scale on the right). The generalization is made for whisker thicknesses varying from 0.5 to 10 μm. The difference from the actual curves does not exceed 20%.

different thickness d, all the results with identical geometry of the experiment can be represented by common curves (Figs. 10, 11)

$$\frac{\Delta\rho^{d}(H)}{\rho^{d}(0)}=\frac{\rho^{d}(H)-\rho^{d}(0)}{\rho^{d}(0)}=F(Hd).$$

In a weak longitudinal field, the experimental curves pass through a maximum situated near $r\approx d$, which does not correspond to the prediction of Ref. 33 according to which the maximum should occur at $r\approx\sqrt{l^{\infty}d}$.

In weak transverse fields $r\approx d$, the increase in the resistance according to the law (18) was observed only for antimony,[37] for zinc and cadmium the experimental dependences are described well by the expression $\Delta\rho^{d}(H)/\rho^{d}(O)\propto H^{2/3}$ (Fig. 12).

In the region $d/2<r<d$, in a field parallel to the flat surface of the whisker, the resistance increases linearly with the field (Fig. 11). The theory predicts a linear drop of the resistance in this section. Finally, in strong fields $2r<d$, the resistance is observed always to increase quadratically with the field. This indicates that the reflection from the surface is not sufficiently specular. Using (16), we shall estimate the lower boundary of the coefficient of diffuseness q from the

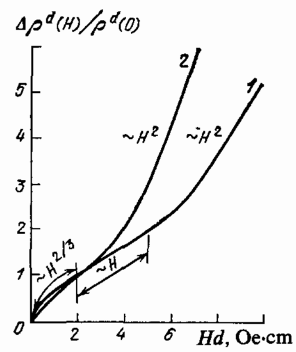

FIG. 11. Generalized experimental curves for the dependence of the resistance of zinc whiskers with a $\langle 12\bar{1}3\rangle$ axis on the transverse magnetic field.[36] $T=4.2$ K. 1-H$\parallel$(0001), 2-H$\parallel\langle 10\bar{1}0\rangle$. The difference from the actual curves for thicknesses ranging from 1.5 to 10 μm does not exceed 20%.

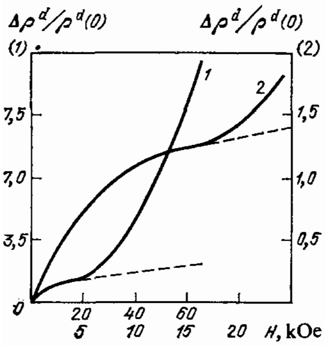

FIG. 12. Dependence of the resistance of a plate-like cadmium whisker on the magnetic field.[36] $T = 4.2$ K; $\mathbf{H} \| \langle 10\bar{1}0\rangle$, $d = 2\,\mu$m. 1-Ordinate axis on the left, value of the magnetic field along the upper scale; 2-ordinate axis on the right, value of the magnetic field along the bottom scale.

condition $ql^\infty \gg r$. Setting $r \approx d$, $l^\infty \approx 10^{-2}$ cm, with $d \approx 10^{-4}$ cm, we have $q \gtrsim 10^{-2}$, which is not a strong requirement.

Thus the size effect in a magnetic field is manifested most distinctly for fields such that $r > d$, where the form of the dependence of the resistance on the magnetic field differs qualitatively from the form for the massive sample. At the same time, the form of the dependence for magnetic fields such that $2r < d$ does not permit drawing conclusions concerning the existence of a static skin effect. However, a comparison of such dependences for different orientation of the field relative to the surface of a plate-like whisker, permits drawing an indirect conclusion supporting its existence. For this purpose, it is best to consider antimony, because in this case there is practically no anisotropy of the resistance in a magnetic field in the massive samples. At the same time plate-like antimony samples, as the measurements show, exhibit strong anisotropy of resistance (Fig. 13). The magnitude of the anisotropy, which can be represented as the ratio $\rho^d_\perp/\rho^d_\|$, increases with the magnetic field, and in strong fields it does not depend on the field, reaching a maximum value (Fig. 14).

From here we can conclude that the scattering by the surface considerably increases the conductivity of the plate in a parallel magnetic field. If the static skin effect is present, then according to expressions (16) and (17) we have

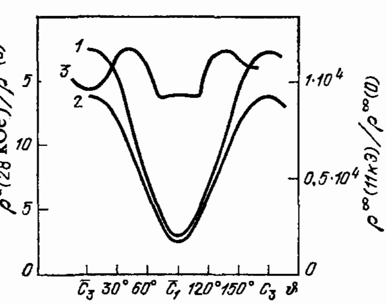

FIG. 13. Anisotropy of the magnetoresistance of antimony specimens.[37] $T = 4.2$ K; $\mathbf{H} \perp \mathbf{I}$, $\mathbf{I} \| \langle C_2\rangle$, φ is the angle between the field and the $\langle C_3\rangle$ axis. 1-Plate-like whisker, thickness $0.14\,\mu$m, width $11\,\mu$m. $H = 28$ kOe, scale on the left, with $\mathbf{H} \| \langle C_1\rangle$ the field parallel to the surface of the plate; 2-same, thickness $0.43\,\mu$m, width 12 mm; 3-massive sample with the same orientation as the plate-like whisker, $H = 11$ kOe, scale on the right.

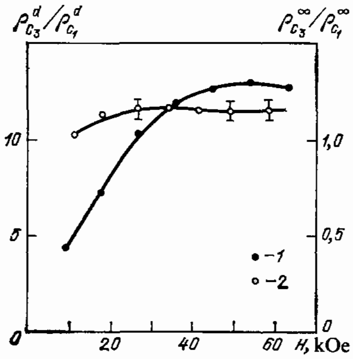

FIG. 14. Dependence of the anisotropy of the magnetoresistance of antimony samples on the magnetic field (see Fig. 13).[37] $T = 4.2$ K. Symbols: 1-plate-like whiskers with thickness $0.14\,\mu$m (scale on the left) with $\mathbf{H} \| \langle C_3\rangle$ and $\mathbf{H} \| \langle C_1\rangle$ the field is perpendicular and parallel to the surface of the plate, respectively; 2-massive antimony sample with the same orientation (scale on the right).

$$\frac{\rho^d_\perp}{\rho^d_\|} \approx \frac{1}{q + (r/l^\infty)} \approx \frac{1}{q} \quad \text{for} \quad \frac{r}{l^\infty} \ll q.$$

This also permits estimating the magnitude of the coefficient of diffuseness q. It turned out that for the thinnest plate-like whiskers of antimony ($d \approx 10^{-5}$ cm) $q < 0.1$. Naturally, this value is averaged over different types of carriers.

The strong anisotropy of the resistance it also observed for plate-like zinc and cadmium whiskers, but it is complicated by the anisotropy related to the existence of open Fermi surfaces in these metals.

b) Temperature dependence of the magnetoresistance of whiskers

Measurements of the dependence of the magnetoresistance on temperature give a direct confirmation of the existence of the static skin effect.

We shall consider the equations of the preceding section for the conductivity and we shall determine for it the sign of the derivatives with respect to the temperature.

In the case when the field H is parallel to the plane of the plate and the relation $r \ll d, l^\infty$ is satisfied, the conductivity of the plate can be represented as

$$\sigma^d = \sigma^s \frac{2r}{d} + \sigma^\infty,$$

where

$$\sigma^s \frac{r}{d} \propto \frac{Ne^2}{p_F} \frac{r}{d} \frac{rl^\infty}{ql^\infty + r}, \quad \sigma^\infty \propto \frac{Ne^2}{p_F} \frac{r^2}{l^\infty}. \tag{20}$$

We shall assume that the coefficient of specularity is constant and that the temperature dependence of the magnetoresistance is determined only by the change in the mean-free path $l^\infty(T)$. Figure 15 shows the dependences $(r/d)\sigma_s(l^\infty)$ and $\sigma^\infty(l^\infty)$ in a constant magnetic field, corresponding to Eqs. (20). The following is evident: a) at low temperatures when $l^\infty \gg d$, $\sigma^d \approx \sigma^s r/d$. Then $\partial\rho^d/\partial T \propto -\partial\sigma^d/\partial T > 0$, i.e., the magnetoresistance increases with temperature; b) at high temperatures $l^\infty \ll d$, $\sigma^d \approx \sigma^\infty$ and $\partial\rho^d/\partial T < 0$, i.e., the magnetoresistance MR decreases with increasing temperature. The transition from the case a) to the case b) corresponds to the condition

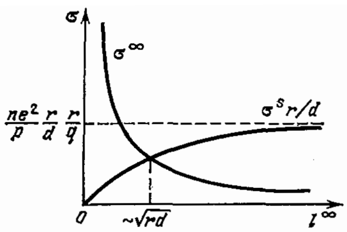

FIG. 15. Theoretical dependences of the surface $\sigma^s r/d$ and volume σ^∞ parts of the conductivity of the sample in a constant magnetic field on the mean-free path of electrons l^∞. The point $l^\infty \approx \sqrt{(rd)}$ corresponds to the condition $(r/d)\partial\sigma^s/\partial l^\infty \approx -\partial\sigma^\infty/\partial l^\infty$ and simultaneously to the condition $(r/d)\sigma^s \approx \sigma^\infty$ with $q < r/l^\infty \ll 1$.

$$-\left(\frac{r}{d}\right)\frac{\partial\sigma^s}{\partial T} = \frac{\partial\sigma^\infty}{\partial T}.$$

The solution of this equation for the condition of weak diffuseness of reflection $q < r/l^\infty \ll 1$ is

$$l^\infty(T) \approx d\left(q + \sqrt{\frac{r}{d}}\right) \approx \sqrt{rd}. \tag{21}$$

For completely diffuse scattering $q = 1$ or in the case of a field perpendicular to the surface of the plate, the surface conductivity does not depend on the temperature:

$$\frac{\sigma^s r}{d} = \frac{Ne^2}{p_F}\frac{r^2}{d}, \quad \frac{\partial\sigma^s}{\partial T} = 0.$$

The temperature dependence of the total conductivity will be determined only by the volume part. For this reason, $\partial\rho^d/\partial T < 0$.

Thus, according to the theory of the static skin effect for plates with high specularity of surfaces, the resistance should behave fundamentally differently from the resistance of the massive sample: as the temperature increases, the resistance in a constant magnetic field under certain conditions must increase. This behavior of the resistance was discovered experimentally in plate-like metal whiskers.[37,38] If the field was perpendicular to the surface of the plate, then the resistance was always observed to drop with increasing temperature, analogously to massive samples (Figs. 16 and 18). With a parallel orientation of the field the resistance at first increases with increasing temperature (Fig. 17), reaches

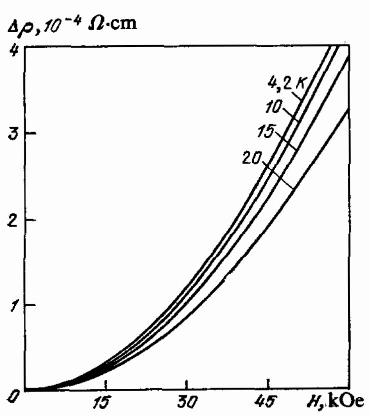

FIG. 16. Dependence of the resistance of a platelike antimony whisker on the magnetic field (H⊥I) for different temperatures (numbers on the curves).[38] The sample is 0.4 μm thick and 52 μm wide. The magnetic field is perpendicular to the plane of the plate. $\Delta\rho^d_H = \rho^d(H) - \rho^d(O)$.

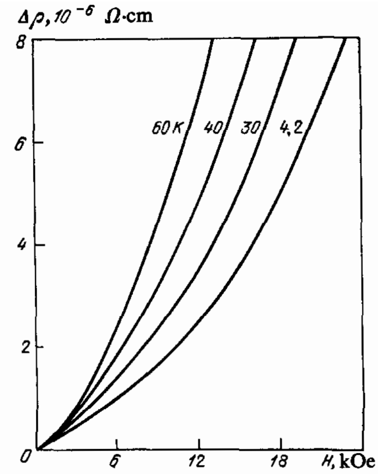

FIG. 17. Same as Fig. 16. Magnetic field parallel to the plane of the plate.

a maximum, and then begins to decrease (Fig. 18).

These results are a serious argument in favor of the static skin effect.

c) Quantum oscillations of the magnetoresistance

A phenomenon whose existence gives incontrovertible proof of the high specularity of reflection of electrons incident on the surface at large angles was discovered for plate-like antimony whiskers. This phenomenon is related to the peculiar quantization of the motion of electrons in a magnetic field under conditions when this motion is restricted by the size of the sample.

The problem of the quantization of the motion of electrons, colliding with one or two bounding surfaces of the plates, in a magnetic field was first raised by Lifshitz and Kosevich.[39] A detailed theory was constructed for electron orbits truncated by two surfaces.[6)]

With specular reflection from surfaces the motion is periodic and must be quantized. Figure 19 shows the area enclosed by a truncated electron orbit and subject to quantization. Since in momentum space this area depends on the magnetic field and the thickness of the sample, the period of the oscillations of thermodynamic and kinetic quantities also depends on the same quantities. Here lies the considerable difference from quantization under the condition $2r < d$, when the period of the oscillations depends only on the area of the extremal sections of the Fermi surface.

It has been shown that in general the periods of quantum oscillations in a thin plate are determined by the following equations[39]:

$$\text{a) } \Delta\left(\frac{1}{H}\right) = \frac{2\pi e\hbar}{c} S_{\text{extr}}^{-1} \quad \text{for } 2r < d,$$
$$\text{b) } \Delta\left(\frac{1}{H}\right) = \frac{2\pi e\hbar}{c}\left|S_{\text{extr}} - H\frac{\partial S_{\text{extr}}}{\partial H}\right|^{-1} \quad \text{for } 2r > d, \tag{22}$$

where S_{extr} in the first case refers to the extremal area of the cross section of the Fermi surface and in the second to the extremal area encompassed by the truncated electron orbits

6)The case of reflection from a single surface in very weak magnetic fields $r \gg d$ was examined in Ref. 40.

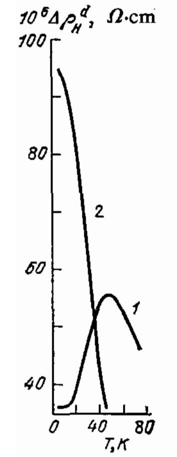

FIG. 18. Dependence of the transverse magnetoresistance ($H = 40$ kOe) of a platelike antimony whisker on temperature.[37] The whisker is 2.5 μm thick, and 110 μm wide. 1-The field H is parallel to the plane of the plate; 2-**H** is perpendicular to the plate.

(Fig. 19). The amplitude of the oscillations should depend on the thickness for any relation between r and d. If $2r = d$, it vanishes for both large and small values of the magnetic field.

For a long time experiments on the observation of the phenomena predicted in Ref. 39 appeared to be unrealistic, since it was generally believed that in metals reflection of electrons from a surface cannot be specular, especially for large angles of incidence. However, after the discovery of the magnetic surface states,[25] high specularity in whiskers and the discovery of the phenomenon of transverse focusing[28] the prejudices against performing such experiments disappeared. The phenomenon was observed in Ref. 41, where antimony whiskers were investigated. The samples had the shape of platelets with a thickness varying form $8\cdot10^{-6}$ to $4\cdot10^{-5}$ cm. The surfaces of the plates were parallel to the basal planes of the crystal. The dependence of the resistance and its derivative with respect to the magnetic field, which was parallel to the surface of the sample, was studied at the temperature of liquid helium. The measuring current flowed in the direction of the binary axis. Oscillations of two types, separated by a distinct boundary, were observed in the experiment: for $H = H_d$ the amplitude of the oscillations of both types vanished (Fig. 20). In fields $H > H_d$ the oscillations represent the Shubnikov–de Haas effect with a period characteristic for massive antimony samples. Oscillations with a single period dominated. In fields $H < H_d$ the oscillations have nothing in common with the usual Shubnikov–de Haas effect: the amplitude of the peaks increases with decreasing field and the distance between them, in this case, increases; for fields in the range $0 < H < H_d$, the number of peaks is much smaller (approximately by a factor of four) than in fields $H > H_d$. When the thickness of the sample decreases, the field H_d increases, the number of new peaks decreases, and they are displaced toward high fields (Fig. 21). These facts indicate that the nature of the oscillations is related to the interaction of electrons with the surface of the sample. The natural assumption was made that both types of oscillations are related to the same group of electrons on the Fermi surface. This permitted comparing the new type of oscillations with the theory.[39] First of all, it was possible to calculate the magnitude of the field for which the dimensions of the electron orbits are comparable to the thickness of the

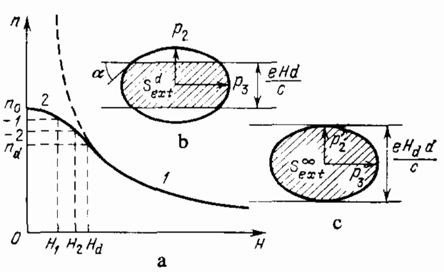

FIG. 19. a) The dependence of the number of flux quanta n on the magnetic field $H > H_d$ (1) (Shubnikov–de Hass effect), 2-$H < H_d$ oscillations on the extremal orbits, truncated by two surfaces of the sample (plate), b) extremal section of the Fermi surface, sectioned by both surfaces of a thin plate of thickness d; c) extremal section in a field equal to the cutoff field $H = H_d$.

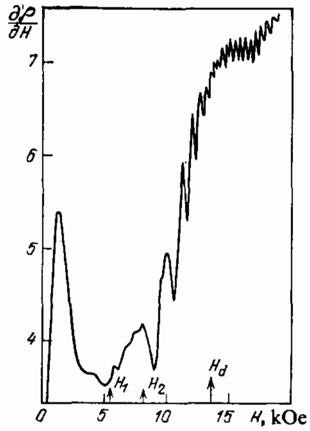

FIG. 20. Dependence of the derivative of the magnetoresistance of the platelike antimony whisker on the magnetic field.[41] The field is parallel to the plane of the plate and perpendicular to the current. $T = 1.4$ K. The specimen is 0.42 μm thick $\partial\rho/\partial H$ is given in arbitrary units. The arrows mark the computed values of the cutoff fields H_d and the fields at the first two peaks H_1 and H_2. For fields $H > H_d$ the oscillations are related to the minimum electron section of the Fermi surface for the orientation $\mathbf{H}\|\langle C_1\rangle$. Their period equals $14.9\cdot10^{-7}$ Oe^{-1}.

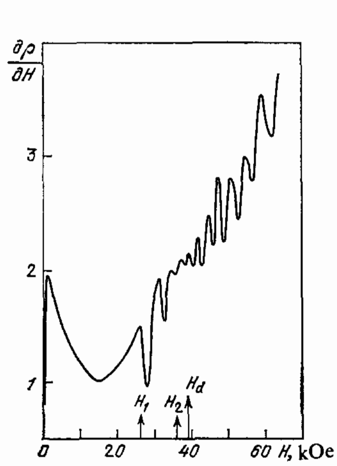

FIG. 21. Same as Fig. 20. $T = 4.2$ K; the sample is 0.14 μm thick.

sample. This can be done by comparing the period of oscillations in fields $H > H_d$ corresponding to the cross section of the Fermi surface of antimony.[42,43] Then (see Fig. 19)

$$H_d = \frac{2p_2c}{ed}.$$

The computed values of H_d coincide well with the experimental magnitudes of fields at which the amplitude of the oscillations vanishes (see Figs. 20 and 21). The position of the new peaks is somewhat more difficult to interpret. The difficulty lies in the fact that even for the thickest sample the number of observed peaks is small: not more than 10, so that it is impossible to speak about the dependence of the period on the magnetic field or thickness and, correspondingly, it is impossible to make comparisons with Eq. (22). However, a qualitative examination of phenomena based on the simplest physical models of the quantization of the motion of electrons in a magnetic field permits estimating the position and number of peaks in the resistance when their number is small.

Let the extremal section of the Fermi surface be an ellipsoid with semiaxes p_2 and p_3. In a field $H = H_d$ the number of flux quanta n through the extremal orbit can be found from the period of the oscillations:

$$n_d = \frac{1}{H_d \Delta (H^{-1})} = \frac{S_{\text{extr}} d}{4\pi\hbar p_2} = \frac{\pi p_2 p_3 d}{4\hbar p_2} = \frac{p_3 d}{4\hbar} \tag{23}$$

As the field decreases, the number n will increase and, in contrast to an unbounded sample, will approach a finite value n_0, where n_0 is determined from the expressions

$$n_0 = \lim_{H \to 0} n = \frac{c}{2\pi\hbar eH} S^d_{\text{extr}}(H), \quad S^d_{\text{extr}}(H) \approx 2p_3 \frac{eHd}{c},$$

from where it follows that

$$n_0 = \frac{p_3 d}{\pi\hbar}. \tag{24}$$

Since the quantum characteristics arise when the number of flux quanta changes by one, the total number of features in the resistance in the interval $O < H < H_d$ will equal

$$\Delta n = n_0 - n_d = \frac{p_3 d}{\pi\hbar} - \frac{p_3 d}{4\hbar} \approx \frac{n_d}{4}. \tag{25}$$

The number Δn determined in this manner agrees well with the number of peaks in the resistance in fields $H < H_d$.

The position of the peaks H_i in fields $H < H_d$ can be found from the condition that the number of flux quanta changes by an integer:

$$\Delta n = n_0 - n(H_i) = i, \quad i = 1, 2, \ldots, \Delta n.$$

For small anisotropy of the shape of the extremal section $p_2 \approx p_3$ the positions of the first and second peaks are determined by the following relation:

$$H_1 \approx \frac{5c}{e} \sqrt{\frac{\pi\hbar p_2^3}{d^3}}; \quad H_2 \approx H_1 \sqrt{2}. \tag{26}$$

The computed values of H_1 and H_2 are marked on the abscissa scales of Figs. 20 and 21. The fairly good agreement with experiment is evident. (It is interesting to note that depending on the shape of the extremal section three cases are possible: $\Delta n > 0$, $\Delta n < 0$, and $\Delta n = 0$.)

All this without doubt indicates that quantization in a magnetic field of truncated electron orbits has been observed, which is possible only under the condition of specular reflection from the surface. It is easy to see that in weak fields the angles of arrival of electrons at the surface will be large. The calculations show that for the first two types of peaks with $d = 0.4\,\mu$m and $\Delta n = 9$ the angles of arrival equal $\alpha_1 \approx 70°$ and $\alpha_2 \approx 50°$.

The observation of quantization in the case of truncated orbits permits solving, in principle, the inverse problem: to reconstruct from the position of the peaks of the oscillations the shape of the extremal section of the Fermi surface and to determine from the amplitude of the oscillations the probability of specular reflection on the angle $W(\alpha)$.

5. CHANGE IN THE ELECTRICAL PROPERTIES OF WHISKERS UNDER A TENSILE STRESS

The high mechanical strength of whiskers, which reaches the limiting theoretical values, gives an exceptional possibility for investigating the influence of anisotropic deformations on the electronic properties of metals.

According to theoretical estimates the rupture strength or the yield stress falls in the range 0.02–0.1 of the magnitudes of the elastic moduli. It is well known how far away from this the actual strength of massive single crystals of pure metals lies. It is lower by two to three orders of magnitude. The reason for such a strong disagreement lies in the existence of different types of defects in the volume and on the surface of the specimens tested.

The lack of defects in the volume and the high degree of perfection of the surface of thin whiskers leads to a strength comparable to the theoretical estimates. Just as for massive specimens, the strength of whiskers is a static property, and there can be a large spread for samples with the same thickness. But, even in the worst case, the strength of micron-thick whiskers is still an order of magnitude higher than the strength of massive crystals. For filamentary whiskers, the highest magnitude of the tensile yield stress reaches 2–5% for different metals.[1] The large magnitude of the elastic deformation, the complete reversibility, and the possibility of continuous variation of the magnitude of this deformation in this respect remove investigations with whiskers from any competition with methods using massive metallic samples. One such investigation is the search for and discovery of transitions of order 2.5.

The theory of 2.5-order transitions was constructed by I. M. Lifshitz in 1960.[44] It is based on the fact that the energy spectrum of conduction electrons in a metal $\varepsilon = \varepsilon(\mathbf{p})$ contains singular points ε_c at which the topology of the isoenergetic surfaces changes. For example, an open surface becomes closed, a new cavity appears, and so on. When $\varepsilon(\mathbf{p}) = \varepsilon_c$, singularities appear in the density of states and near ε_c the dynamics of electrons has an anomalous character. It has been shown that if a continuously varying external parameter exists, during whose measurement the Fermi energy reaches the value ε_c, then the singularities in the density of states and the dynamics of the electrons lead to peculiar anomalies in the thermodynamic and kinetic characteristics of the metal. I. M. Lifshitz suggested that such anomalies be called transitions of order 2.5. It is significant that these transitions are not related to the change in the symmetry of the crystal lattice or to a significant change in the number of conduction electrons.[7)] The continuously varying parameters could be different types of deformations, the magnetic field, and impurities.

The new unusual changes in the properties of metals predicted in Ref. 44 stimulated an intensive experimental search for transitions of order 2.5. The correct check of the predictions of the theory entailed the observation of some anomaly in the properties of the metal and the establishment of a relation between this anomaly and the change in the topology of the Fermi surface. The latter is necessary because anomalies can also arise due to other factors, for example, changes in the phonon spectrum.

The method of investigation with large quasistatic pressures and low temperatures has been widely used.[46] This method was used to produce a topological transition in pure cadmium under pressures exceeding 9 kbar.[47]

Anomalies in the dependence of the temperature of the superconducting transition on pressure were observed in a number of other investigations in thallium[48] and in rhenium.[49] The authors proposed as one of the possible explanations the existence of topological changes of the Fermi surfaces of these metals under pressure.

For a long time Ref. 50 was the only work in which the change in the volume of the Fermi surface accompanying a change in pressure was associated with the appearance of anomalies in the galvanomagnetic properties of bismuth alloys and it was concluded that a transition of order 2.5 was observed. The small number of such experimental works is related to the fact that in investigations of transitions of order 2.5, problems associated with the continuous variation of the parameter describing the action on the single crystal, complete reversibility, and reproducibility of the results play the determining role. It is also important that the method allow following simultaneously the change in the topology of the Fermi surface.

One of the first works in which whiskers were used to observe the change in the topology of the Fermi surface under tension was Ref. 51. Quite thick iron whiskers ($d = 0.3$ mm) were investigated. The Fermi surface of iron is open in the directions $\langle 100\rangle$ and $\langle 110\rangle$. This is manifested, in particular, in the fact that the angular dependences of the magnetoresistance have narrow deep minima. The dependence of the depth of these minima on the magnitude of the elongation of the whisker under tension was studied. The results are shown in Fig. 22. It is evident that as the samples are elongated the depth of the minima decreases. Complete vanishing of the minima in the magnetoresistance would indicate the vanishing of open sections of the Fermi surface, i.e., a change in its topology. Such a change, if the experimental results are extrapolated, should occur with a relative elongation of the sample along the axis [111] by 0.5%. Such elongations were not achieved in this work.

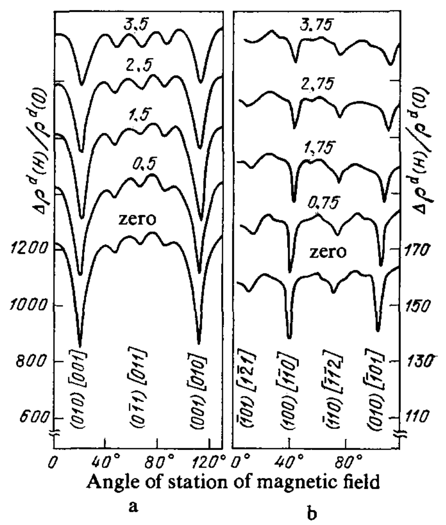

FIG. 22. Anisotropy of the transverse resistance of filamentary iron whiskers in a field of $H = 120$ kOe as a function of the tension force.[51] $T = 4.2$ K. a) Dimensions of the specimen: $0.26\times0.24\times8$ mm^3 (the tensile load is applied along the [110] axis; the 3.5-kg load corresponds to a relative elongation of the sample by 0.26%); b) sample thickness of 0.34 mm (tension load applied along the [111] axis; the 3.75-kg load corresponds to a relative elongation of the sample by 0.25%). The indices at the minima indicate the following: in parentheses the orientation of the H field and in the brackets the orientation of the open orbit. For clarity, each successive curve for increasing load is displaced along the vertical by the same amount.

Analogous investigations were performed in work on zinc whiskers.[52] Whiskers with a thickness of 1–2 μm were measured. The Fermi surface of zinc contains open sections, parallel to the basal plane (0001), and an open direction along the [0001] axis. In both these cases, the layer of open sections of the Fermi surface is quite thin. This suggested that they will disappear with elongation. A change in the anisotropy of the magnetoresistance accompanying elongation of the samples was observed in the work. The results are shown in Fig. 23. The minimum of the resistance in the curves presented with the field orientation being $\mathbf{H}\|(0001)$ is related to the existence of a narrow layer of open sections oriented along the [0001] axis. With a large elongation of the whisker the minimum disappears. This indicates that bridges in the Fermi surface of zinc are ruptured along the [0001] axis. As is evident in Fig. 24, this occurs when the sample is elongated by 0.4%. In other respects, the form of the anisotropy of the resistance does not change significantly. The nature of the dependence of the magnetoresistance on the extension of the specimen corresponds qualitatively to the case examined in Ref. 44 with a transition of the open Fermi surface, with compensated electronic and hole volumes, into a closed surface: a marked rise in the resistance as the critical value of the elongation is approached and a weak

[7)]The concept of a 2.5-order transition was subsequently extended. Transitions with total vanishing of charge carriers in the conduction bands (i.e., the total volume of the Fermi surface vanishes) were included in it. This permitted including transitions of the type metal–semiconductor and semiconductor–semimetal amongst 2.5-order transitions. Such transitions have been observed.[45] Here, we remain within the framework of the initial definition of a 2.5-order transition given in Ref. 44, for which the change in the topology of the Fermi surface with its total volume remaining constant in the vicinity of the transition is significant.

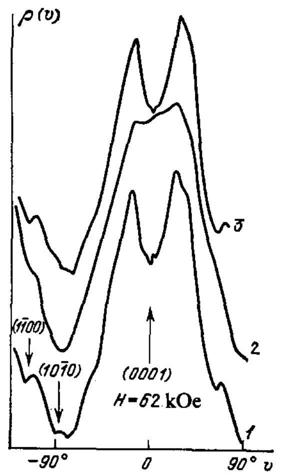

FIG. 23. Anisotropy of the transverse magnetoresistance of a platelike zinc whisker as a function of the magnitude of the relative elongation.[52] $T = 4.2$ K, $H = 62$ kOe, thickness 1.5 μm. The elongation and current are oriented along the [$2\bar{3}11$] axis. 1-Initial state, elongation equal zero; 2-elongation equals 1%, 3-final state, load removed, elongation equals zero. The resistance is shown in arbitrary units. For clarity, curves 2 and 3 are displaced along the vertical.

dependence of the resistance on the elongation after the critical value is attained (Fig. 24).

If the Fermi surface of the metal is closed, and the topological transition is not related to the appearance of open sections, then it is possible to draw conclusions concerning a change in the topology of the Fermi surface only on the basis of measurements of the geometric characteristics of the Fermi surface. In the case of whiskers, the only method for this purpose is the measurement of the frequencies of quantum oscillations in phenomena of the Shubnikov–de Haas type. The disappearance or appearance of new oscillation frequencies at a definite value of the deformation must indicate the disappearance or appearance of new cavities in the Fermi surface. This method was used to observe transitions of order 2.5 in bismuth with a simple tensile stress, to which samples of filamentary whiskers of thickness ≈ 1 μm were subjected.[53] The transition was observed for one of two whisker orientations investigated. It was observed by the vanishing of the frequencies of quantum oscillations of the resistance, related to one of the three electron ellipsoids of the Fermi

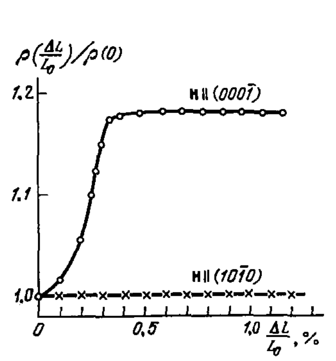

FIG. 24. Dependence of the transverse magnetoresistance for the same whisker (see Fig. 23) on the magnitude of the relative elongation for two orientations of the magnetic field $H = 62$ kOe. $\Delta L/L_0 = (L - L_0)/L_0$; L and L_0 are the lengths of the specimens with and without a load.

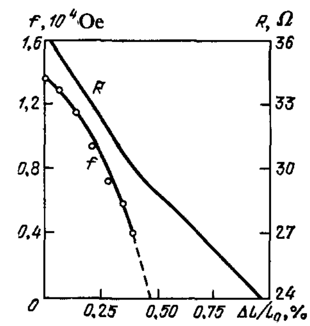

FIG. 25. Dependence of the resistance R ($H = 0$) and frequency f of quantum oscillations of the magnetoresistance of a filamentary bismuth whisker on the relative elongation of the specimen.[53] $T = 4.2$ K. The axis of the sample forms an angle of 78° with the trigonal axis and 12° with the binary plane of the crystal. The sample is 1.6 μm thick. The values of the frequencies f were obtained with fixed elongations. The resistance is recorded automatically under continuous elongation.

surface of bismuth (Fig. 25). The vanishing occurs at an elongation of the specimen of approximately 0.5%. After the transition, the Fermi surface consists of two electron ellipsoids and one hole ellipsoid.

Simultaneously with the observation of the change in the frequencies of quantum oscillations in the same sample, the change in the resistance without a magnetic field was measured. It was found that in the region of the topological transition, the resistance exhibits a break (Fig. 25), which agrees with the theory.[44]

The most complete investigation of a 2.5-order transition was performed in Ref. 54 on micron-thick aluminum whiskers subjected to a tensile stress. The frequencies of quantum oscillations of the thermo-emf, of the resistance without the magnetic field, and of the temperature of the superconducting transition T_c were measured simultaneously (Fig. 26). It was found that under tension along the

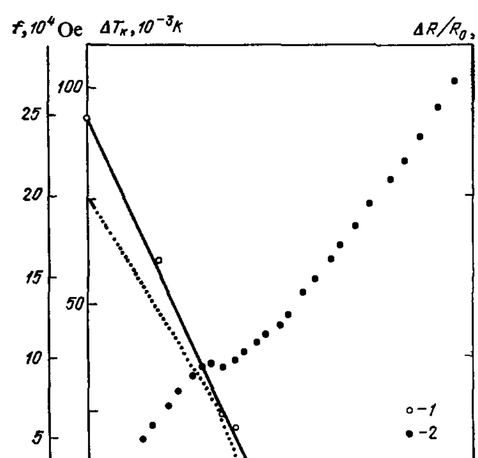

FIG. 26. Dependence of the frequencies f of quantum oscillations of the thermo-emf, change in the temperature of the superconducting transition T_c and the resistance R as a function of the elongation of an aluminum whisker.[54] $d = 1$ μm. 1-frequency f; 2-increment to the temperature of the superconducting transition ΔT_c. The dotted curve shows the relative decrease of the resistance, $T = 2$ K.

[0111] axis, with elongations of about 0.5%, the frequencies of oscillations related to the minimal cross sections of the electron part of the Fermi surface in the third Brillouin zone vanish. This part is nearly ring-shaped. Under tension the "ring" ruptures at four equivalent locations, forming four separate cavities. For the same magnitude of the elongation (0.5%), just as in Ref. 53, a break was observed in bismuth whiskers in the dependence of the resistance on the elongation. It was first shown experimentally in Ref 54 that the appearance of anomalies in the dependence of T_c on the stress is directly correlated with the change in the topology of the Fermi surface.

6. CONCLUSIONS

The investigations carried out thus far have been performed on whiskers not much less than 1 μm thick. The region of thicknesses less than 0.1 μm remains, for the time being, completely unstudied. In this region, new phenomena, related to the quantum size effect, can be expected in whiskers, since the thickness of the samples can be comparable to the de Broglie wavelength of the conduction electrons. There are technical difficulties here, related to mechanical and electrical mounting of superthin whiskers. The magnetic properties of thin whiskers remain unstudied. Progress in this direction has been made very recently. An exceptionally elegant magnetometer for investigating the magnetic properties of such miniature objects as whiskers with a volume of up to 10^{-9} cm^3 has been developed.[55] The sensitive element of this magnetometer is the object of investigation itself—the thin whisker.

The example with the magnetometer makes us hopeful that the last word has not yet been said in the investigation of the properties of whiskers and that further investigation of these exquisite crystals will contribute much useful information to science.

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Translated by M. E. Alferieff