Theory of residual resistance of a metallic bicrystal

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The resistance of the boundary between crystallites to direct current flowing in a direction normal to the boundary plane is investigated theoretically. The scattering of the electrons by the boundary between two crystallites is described phenomenologically with the aid of the concepts of diffusivity and specularity, modified as applied to the description of scattering by an internal boundary in a metal. The effect of disorientation of the crysallites is due to the allowance for the anisotropy of the dispersion law. The resistance of a diffusely scattering boundary is $\mathscr{R}\approx 0.3l/\sigma_0$ (l is the mean free path and σ_0 is the electric conductivity of the bullk metal). The resistance of a speculrly reflecting and refracting boundary, in the actual case of small disorientation angles δ, is proportional to $(l/\sigma_0)\ \delta^2\ln(1/|\delta|)$. The fraction of the grain boundaries in the residual resistance of a polycrystal is of the order of l/d (d is the grain dimension).

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The crystallite separation boundaries (grain boundaries) in polycrystals, as well as the block (subgrain) boundaries, offer resistance to electric current primarily because various kinds of defects, primarily dislocations, are concentrated on them. In addition, because of the disorientation of the individual crystallites, an electron moving through such a boundary changes its direction, as a result of which a resistance effect can arise again. A reliable calculation of the resistance of grain boundaries, at the microscopic level, is difficult because of the great variety of microscopic models of the boundaries. It is therefore quite advantageous to investigate the resistance phenomenologically with account taken of the disorientation of neighboring crystals, by modifying the prevailing concepts concerning diffuse and specular scattering of electrons from a boundary between a metal and vacuum.

To this end we investigate the flow of direct current through a metallic bicrystal consisting of two single crystals of one and the same metal, and disoriented arbitrarily relative to each other. We assume that the single crystals are joined along some plane (xy, see Fig. 1) which is arbitrarily oriented relative to the crystallographic axes of both crystals. Since we are studying the resistance of a boundary between crystallites, we can disregard for simplicity the influence of the external boundaries of the sample, i.e., assume that the bicrystal occupies all of space. The temperature is assumed to be zero, since principal interest attaches to the residual resistance of the boundary.

It is technically convenient to assume the given quantity to be the component of the current density normal to the boundary, i.e., the z-component j_0. The quantity j_0 is assumed to be independent of the time and of the coordinates. The sought quantity is the distribution of the electric field intensity $\mathbf{E}(x, y, z)$. Knowledge of this distribution makes it possible to calculate the resistance of the bicrystal and, in particular, to separate the resistance of the boundary. Incidentally, when solving the problem we can find the tangential (relative to the boundary) components of the current density.

1. FUNDAMENTAL EQUATIONS AND CALCULATION FORMULAS

Maxwell's equations for a conductor carrying a stationary current take the form

$$\operatorname{rot}\mathbf{E}=0,\quad \operatorname{div}\mathbf{j}=0. \tag{1}$$

These equations must be written for the left-hand and right-hand crystals and, in addition, supplemented by the standard boundary conditions, namely continuity of the z component of the current density and of the x and y components of the electric field. The homogeneity of the physical conditions along the xy plane leads to the requirement

$$j_z^{(1)}=j_z^{(2)}=\text{const}. \tag{2}$$

The indices 1 and 2 label quantities pertaining to the left and right crystallites, respectively. The first equation of (1) and the boundary conditions for it are satisfied if we assume only the z component of the field to be different from zero:

$$\mathbf{E}^{(1)}=(0,\ 0,\ E_1(z)),\quad \mathbf{E}^{(2)}=(0,\ 0,\ E_2(z)). \tag{3}$$

The system (1) must be supplemented by a material equation that describes the connection between the current and the field. In the simplest case this connection is local:

$$j_i^{(\nu)}=\sigma_{ik}^{(\nu)}E_k^{(\nu)},\quad \nu=(1,2). \tag{4}$$

However, if we confine ourselves to the local connection between the current and the field, then the resis-

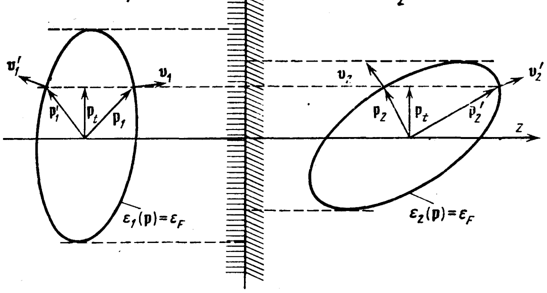

FIG. 1.

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tance of the boundary vanishes automatically, and the calculation of the resistance of a bicrystal becomes a trivial problem of calculating the resistance of series-connected conductors, each of known resistance. We must therefore write down the nonlocal connection between the current and the field, which can be obtained by solving the kinetic equation for the electron distribution function $f(\mathbf{p}, z)$. The distribution function is linearized in the usual manner:

$$f(\mathbf{p}, z) = f_0(\varepsilon(\mathbf{p})) - e\frac{\partial f_0}{\partial \varepsilon}\psi(\mathbf{p}, z). \tag{5}$$

Here e is the electron charge, f_0 is the equilibrium Fermi distribution function, and $\psi(\mathbf{p}, z)$ is the sought function which we call for brevity the nonequilibrium increment. It is small to the extent that the electric field is small. The dependence of the electron energy ε on the quasimomentum $\mathbf{p}$ is the best chosen as simple as possible, to simplify the calculations, but at the same time it must reflect the anisotropy of the metal. These requirements are satisfied by the quadratic anisotropic dispersion law:

$$\varepsilon(\mathbf{p}) = \frac{1}{2m}\gamma_{ik}p_ip_k. \tag{6}$$

It is convenient to choose the average effective mass m in such a way that the determinant of the dimensionless matrix $\|\gamma_{ik}\|$ becomes equal to unity. The effective-mass anisotropy, described by the tensor γ_{ik}, plays in this case the principal role, inasmuch as in the isotropic model the difference between the grains vanishes.

At zero temperature, the derivative $\gamma f_0/\gamma\varepsilon$ is a δ function; consequently, in the formulas that follow, the quasimomenta $\mathbf{p}$ are such that their ends lie on Fermi surfaces $\varepsilon_F = \varepsilon(\mathbf{p})$ in the form of ellipsoids with different orientations in each crystallite relative to the laboratory frame connected with the boundary. The equations of the Fermi ellipsoids are

$$\frac{1}{2m}\gamma_{ik}^{(1)}p_ip_k = \varepsilon_F, \quad \frac{1}{2m}\gamma_{ik}^{(2)}p_ip_k = \varepsilon_F. \tag{7}$$

The connection between the tensors $\hat{\gamma}^{(1)}$ and $\hat{\gamma}^{(2)}$ is given by

$$\gamma_{ik}^{(2)} = \alpha_{ij}\alpha_{kl}\gamma_{jl}^{(1)}, \tag{8}$$

and the rotation matrix $\hat{\alpha}$ is defined in the general case by three parameters (for example, by Euler angles).

If we describe the scattering of the electrons in the interior of each crystallite in the τ approximation (we assume $\tau_1 = \tau_2 = \tau$), then the kinetic equations are written in the known form

$$v^{(\nu)}\frac{\partial\psi^{(\nu)}(z, \mathbf{p})}{\partial z} + \frac{1}{\tau}\psi^{(\nu)}(z, \mathbf{p}) = v_z^{(\nu)}E_z^{(\nu)}(z), \quad \nu = 1, 2. \tag{9}$$

Here $\mathbf{v} = \partial\varepsilon/\partial\mathbf{p}$ is the electron velocity. The electric field in each of the crystallites has obviously homogeneous components $E_z^{(\nu)} \equiv E_\nu$, which are obtained by dividing the current density j_0 by the components $\sigma_{zz}^{(\nu)}$ of the electric conductivity of each of the media:

$$E_\nu = j_0/\sigma_{zz}^{(\nu)}. \tag{10}$$

The quantities $\sigma_{zz}^{(\nu)}$ are determined by the known method, if it is noted that at large distances (compared with the mean free path) from the boundary the solutions of the kinetic equations (9) take the form

$$\psi^{(\nu)}(z, \mathbf{p}) \approx v_z^{(\nu)}\tau E_\nu, \quad |z| \to \infty. \tag{11}$$

With the aid of (11) we obtain

$$\sigma_{zz}^{(\nu)} = \gamma_{33}^{(\nu)}\sigma_0, \quad \sigma_0 = \frac{8\pi}{3}\frac{e^2p_F{}^2l}{(2\pi\hbar)^3}. \tag{12}$$

We have introduced here the following notation: $p_F = (2m\varepsilon_F)^{1/2} = mv_F$ is the Fermi momentum and $l = v_F\tau$ is the electron mean free path.

To separate the homogeneous components, the field distribution must be represented in the form

$$E_z^{(\nu)}(z) \equiv E_\nu(z) = E_\nu - d\varphi_\nu(z)/dz, \quad \nu = 1, 2. \tag{13}$$

The sought quantities are now the potentials $\varphi_\nu(z)$, which vanish at infinity.[1)] Their appearance is due to collisions between the electrons and the boundary. The resistance of the boundary (per unit area) is expressed in terms of the jump of the additional potential φ_ν. The corresponding equation for the total resistance $\mathscr{R}_{\text{tot}}$ of the bicrystal is obtained by calculating the Joule losses:

$$\mathscr{R}_{tot} = L_1/\sigma_{zz}^{(1)} + L_2/\sigma_{zz}^{(2)} + [\varphi_2(0) - \varphi_1(0)]/j_0. \tag{14}$$

The first two terms are the resistances of the crystallites taken separately (L_1 and L_2 are their dimensions in the z direction) and are of no interest at present. The third term is in fact that boundary resistance due to the discontinuity of the potential φ_ν on the boundary:

$$\mathscr{R} = [\varphi_2(0) - \varphi_1(0)]/j_0. \tag{15}$$

Of course, the presence of the discontinuity φ_ν is due to the zero thickness of the boundary. The physically small parameter is the ratio of the thickness of the boundary to the mean free path, and we consider in the problem the zeroth approximation in terms of this parameter. The discontinuity, naturally, is proportional to j_0 and therefore the resistance is determined only by the structure of the boundary and by the character of the scattering of electrons from it.

If we regard (for the time being) the potentials $\varphi_\nu(z)$ as specified functions of the coordinate, then the general solutions of the first-order differential equations (9) can be easily found. The general solution contains one arbitrary constant A for each fixed $\mathbf{p}$. Consequently, to describe the solution for arbitrary $\mathbf{p}$ it is necessary to introduce the arbitrary function $A(\mathbf{p})$. The boundary condition at infinity (11) separates the electrons in each of the crystallites into two groups: those moving away from the boundary and those moving towards the boundary. Each group is described by its own distribution function, with the function $A(\mathbf{p})$ determined by the boundary condition at infinity and by the condition on the crystallite boundary, respectively, for the electrons moving towards and away from the boundary. We have at $z < 0$

$$\psi_1(z, \mathbf{p}) = -\varphi_1(z) + v_1\tau E_1 + \frac{1}{v_1\tau}\int_{-\infty}^{z}\varphi_1(z')\exp\left(-\frac{z-z'}{v_1\tau}\right)dz', \quad v_z^{(1)}(\mathbf{p}) > 0, \tag{16a}$$

$$\psi_1(z, \mathbf{p}) = A_1(\mathbf{p})\exp\left(\frac{z}{v_1\tau}\right) - \varphi_1(z) - v_1\tau E_1\left(1 - \exp\left(\frac{z}{v_1\tau}\right)\right) - \frac{1}{v_1\tau}\int_0^z\varphi_1(z')\exp\left(\frac{z-z'}{v_1\tau}\right)dz', \quad v_z^{(1)}(\mathbf{p}) < 0$$

and at $z > 0$

$$\psi_2(z, \mathbf{p}) = \begin{cases} A_2(\mathbf{p}) \exp\left(-\frac{z}{v_2\tau}\right) - \varphi_2(z) + v_2\tau E_2\left(1 - \exp\left(-\frac{z}{v_2\tau}\right)\right) \\ + \frac{1}{v_2\tau} \int_0^z \varphi_2(z') \exp\left(-\frac{z-z'}{v_2\tau}\right) dz', & v_z^{(2)}(\mathbf{p}) > 0; \\ -\varphi_2(z) - v_2\tau E_2 + \frac{1}{v_2\tau} \int_z^\infty \varphi_2(z') \exp\left(\frac{z-z'}{v_2\tau}\right) dz'; & v_z^{(2)}(\mathbf{p}) < 0. \end{cases} \tag{16b}$$

We have introduced in these equations the notation $v_\nu(\mathbf{p}) \equiv |v_{2z}^{(\nu)}(\mathbf{p})|$, i.e., the quantities v_1 and v_2 are nonnegative.

Knowledge of the distribution functions enables us to find the current density at an arbitrary point of the sample. At zero temperature, the coefficient of $\psi(\mathbf{p}, z)$ in (5) contains a δ function in energy. Therefore integration over momentum space, which is needed to calculate the current, reduces to integration over the Fermi surface, and the latter reduces to integration over the projection Σ of the Fermi surface on the plane xy (we are calculating in fact only the z component of the current density). If we denote by $\psi^{\pm}(\mathbf{p}, z)$ the increments corresponding to the electrons with positive and negative z-components of the velocities, then we have

$$j_z^{(\nu)} = \frac{2e^2}{(2\pi\hbar)^3} \iint_{\Sigma_\nu} dp_x\, dp_y [\psi_\nu^+(\mathbf{p}, z) - \psi_\nu^-(\mathbf{p}, z)]. \tag{17}$$

The quasimomentum component p_z is assumed here to be expressed here in terms of p_x, p_y, and ε_F, inasmuch as the end of the vector $\mathbf{p}$ is situated on the Fermi surface. Using (16) and (17), we get

$$j_z^{(1)} = j_0 = \frac{2e^2}{(2\pi\hbar)^3} \iint_{\Sigma_1} dp_x\, dp_y \left\{ -A_1(\mathbf{p}) \exp\left(\frac{z}{v_1\tau}\right) + v_1\tau E_1 \left[2 - \exp\left(\frac{z}{v_1\tau}\right)\right] + \frac{1}{v_1\tau} \left[\int_{-\infty}^{z} \varphi_1(z') \exp\left(-\frac{z-z'}{v_1\tau}\right) dz' + \int_0^z \varphi_1(z') \exp\left(\frac{z-z'}{v_1\tau}\right) dz' \right] \right\}, \quad z < 0. \tag{18}$$

$$j_z^{(2)} = j_0 = \frac{2e^2}{(2\pi\hbar)^3} \iint_{\Sigma_2} dp_x\, dp_y \left\{ A_2(\mathbf{p}) \exp\left(-\frac{z}{v_2\tau}\right) + v_2\tau E_2 \left[2 - \exp\left(-\frac{z}{v_2\tau}\right)\right] + \frac{1}{v_2\tau} \left[\int_0 \varphi_2(z') \exp\left(-\frac{z-z'}{v_2\tau}\right) dz' - \int_z^\infty \varphi_2(z') \exp\left(\frac{z-z'}{v_2\tau}\right) dz' \right] \right\}, \quad z > 0. \tag{19}$$

Since the z component of the current density is a constant (j_0) independent of z, it follows that for given $A_1(\mathbf{p})$ and $A_2(\mathbf{p})$ Eqs. (18) and (19) constitute jointly a system of integral equations with respect to the potentials $\varphi_1(z)$ at $\varphi_2(z)$. Solution of this system makes it possible, in particular, to find the discontinuity $\varphi_2(0) - \varphi_1(0)$ of the potential on the crystallite separation boundary and with it, in accordance with (15), the resistance of the boundary.

The condition that the z component of the current density be homogeneous leads to the well known (see, e.g., Ref. 1) electroneutrality condition

$$\int d\mathbf{p}[f(\mathbf{p}, z) - f_0(\varepsilon)] = 0. \tag{20}$$

To verify this, it suffices to integrate both halves of (9) with respect to the momenta. The same result is obtained if both halves of (18) and (19) are differentiated with respect to z. The system obtained by differentiating (18) and (19), i.e., written down using directly the electro-neutrality condition, is technically more convenient to solve than the initial system. We write down this system in the form

$$\iint_{\Sigma_1} dp_x\, dp_y \left[-\frac{A_1(\mathbf{p})}{v_1\tau} \exp\left(\frac{z}{v_1\tau}\right) - E_1 \exp\left(\frac{z}{v_1\tau}\right) + \frac{2}{v_1\tau} \varphi_1(z) - \frac{1}{(v_1\tau)^2} \int_{-\infty}^{0} \varphi_1(z') \exp\left(-\frac{|z-z'|}{v_1\tau}\right) dz' \right] = 0; \quad z < 0. \tag{21}$$

$$\iint_{\Sigma_2} dp_x\, dp_y \left[-\frac{A_2(\mathbf{p})}{v_2\tau} \exp\left(-\frac{z}{v_2\tau}\right) + E_2 \exp\left(-\frac{z}{v_2\tau}\right) + \frac{2}{v_2\tau} \varphi_2(z) - \frac{1}{(v_2\tau)^2} \int_0^\infty \varphi_2(z') \exp\left(-\frac{|z-z'|}{v_2\tau}\right) dz' \right] = 0; \quad z > 0. \tag{22}$$

The method of solving the system (21) and (22) is determined by the concrete form of the dispersion law and by the functions $A_1(\mathbf{p})$ and $A_2(\mathbf{p})$. As was already noted, the dispersion law is chosen in the form (6). As to the functions $A_1(\mathbf{p})$ and $A_2(\mathbf{p})$, to determine them it is necessary to make some assumption concerning the character of the scattering of the electrons by the boundary. We consider separately two limiting cases: diffuse and specular scattering.

2. RESISTANCE OF GRAIN BOUNDARY IN DIFFUSE SCATTERING

Scattering is said to be diffuse when the electron has equal probability of being scattered in all directions. In other words, the distribution function of the electrons that move away from the surface does not depend on the direction of the momentum after the scattering:

$$\psi_2^+(0, \mathbf{p}) = C_2, \tag{23}$$

$$\psi_1^-(0, \mathbf{p}) = C_1. \tag{24}$$

The use of Eqs. (16) allows us to conclude that in this case the functions $A_1(\mathbf{p})$ and $A_2(\mathbf{p})$ turn into constants:

$$A_1(\mathbf{p}) = A_1, \quad A_2(\mathbf{p}) = A_2. \tag{25}$$

The physical meaning of these constants is that they determine the renormalization $\Delta\mu$ of the chemical potential of the electrons that move away from the surface:

$$e(A_\nu - \varphi_\nu(0)) = \Delta\mu_\nu. \tag{26}$$

The values of the constants A_1 and A_2 are obtained by using Eqs. (18) and (19) with $z = 0$.

Since A_1 and A_2 are constants, the system (21) and (22) breaks up into two independent equations. These equations can be written in rather simple form, using the following circumstances. At the chosen quadratic dispersion law, the dependence of the z component of the velocity on the x and y components of the momentum is written in the form

$$v_\nu = \frac{1}{m} [\gamma_{33}^{(\nu)} p_F^2 - (\gamma_{22}^{(\nu)})^{-1} p_x^2 + 2(\gamma_{12}^{(\nu)})^{-1} p_x p_y - (\gamma_{11}^{(\nu)})^{-1} p_y^2]^{1/2} \tag{27}$$

where $(\gamma_{ik}^{(\nu)})^{-1}$ is the element of the matrix inverse to $\|_{ik}\|$. The regions Σ_1 and Σ_2 are the interiors of ellipses whose equations are obtained by equating to zero the radicands in (27). Integration of the functions contained in (21) and (22) over these regions is elementary and leads to the appearance of the integral exponentials

$$\mathscr{E}_n(s)=\int_0^1 dx\, x^{n-2}\exp(-s/x). \tag{28}$$

If we go over in (22) to the dimensionless coordinate and to the dimensionless potential $\chi_2(s)$:

$$s=z/l\sqrt{\gamma_{33}^{(2)}},\quad \chi_2(s)=(j_0l)^{-1}\sigma_0\varphi_2(z)\sqrt{\gamma_{33}^{(2)}},$$

then we obtain from (22) for the function $\chi_2(s)$ an equation that contains no parameters:

$$\chi_2(s)-\frac{1}{2}\int_0^\infty\chi_2(s')\mathscr{E}_1(|s-s'|)ds'-\mathscr{E}_2(s)\int_0^\infty\chi_2(s')\mathscr{E}_2(s')ds'$$
$$=\frac{1}{3}\mathscr{E}_2(s)-\frac{1}{2}\mathscr{E}_3(s). \tag{29}$$

A similar equation is obtained (after a suitable transition to dimensionless variables) also for $\chi_1(s)$, with $\chi_1(s)=-\chi_2(-s)$. As a net result, taking (15) into account, the resistance of the boundary turns out to be

$$\mathscr{R}=\frac{l}{\sigma_0}\left(\frac{1}{\sqrt{\gamma_{33}^{(1)}}}+\frac{1}{\sqrt{\gamma_{33}^{(2)}}}\right)\chi_2(0). \tag{30}$$

As seen from (30), in diffuse scattering the resistance does not depend on the electron mean free path in the interior of the metal (since σ_0 is proportional to l) and depends relatively weakly on the orientation of the crystallites (to the extent that the quantities $\gamma_{33}^{(\nu)}$ change). In the absence of disorientation of the grains, the resistance does not vanish, since the scattering introduced in this model "by brute force" still remains. In order of magnitude, the resistance of the boundary coincides with the resistance of a layer of metal of thickness l. Therefore the relative contribution of the diffusely scattering boundaries to the total resistance of the metal is of the order of l/d (d is the dimension of the grain in the polycrystal). This contribution constitutes a unique size effect connected with the internal boundaries in polycrystalline samples.

As to the constant $\chi_2(0)$, general considerations connected with its determination from the solution of Eq. (29), which contains no parameters, shows that this constant should be of the order of unity. At the same time it is possible to obtain an exact integral representation of this constant. Basic to its determination is the directly verifiable fact that the solution of (29) is of the form

$$\chi_2(s)=s+a+f(s), \tag{31}$$

where a is an arbitrary constant and $f(s)$ is the solution of the homogeneous Milne equation, which is well known in the literature:

$$f(x)-\frac{1}{2}\int_0^\infty\mathscr{E}_1(|x-y|)f(y)dy=0. \tag{32}$$

Wiener and Hopf (see, e.g., Ref. 2) have shown that the solution of Milne's equation can be written in the form

$$f(x)=C(x+b+g(x)), \tag{33}$$

where C is an arbitrary constant b is a determined constant, and the function $g(x)$ decreases exponentially at infinity.

By choosing the constants C and a it is possible to make the function $\chi_2(s)$ decrease at infinity. Thus, the determination of $\chi_2(0)$ reduces to a determination of such a solution of Milne's equation, in which the leading term of the asymptotic form at infinity is $-x$. Then $\chi_2(0)=-g(0)$. To find $g(0)$ we must solve the Milne equation by the Weiner-Hopf method. The standard factorization procedure leads ultimately to the result

$$\chi_2(0)=\frac{1}{\pi}\int_0^{\pi/2}\left(\frac{3}{\sin^2 x}-\frac{1}{1-x\operatorname{ctg}x}\right)dx-\frac{1}{\sqrt{3}}\cong 0.15. \tag{34}$$

The constant $\chi_2(0)$ thus turns out to be different from zero and positive, as it should, since resistance is positive.

The physical cause of the boundary resistance is the stopping of the electrons by the boundary, and, as a consequence, of the appearance of an electric double layer on the boundary. When current flows from left to right in the right-hand crystal, an excess negative charge is produced with a density that varies in proportion to $1/|z|$. Speaking more accurately, by differentiating the potential twice with respect to z we obtain for the excess charge density $\Delta\rho$ the expression (at $|z|/l\ll 1$)

$$\Delta\rho^{(\nu)}(z)=-j_0/8\pi\sqrt{3}\,\sigma_0\gamma_{33}^{(\nu)}z. \tag{35}$$

Accordingly, the field increases logarithmically as $|z|\to 0$. It must be borne in mind, of course, that the inequality $|z|\gg a$ must be satisfied, where a is the interatomic distance. At $|z|/l\gg 1$ the excess density is exponentially small, and at $|z|\sim l$ it is of the order of $\Delta\rho\sim\rho_a(a/l)^2(v_D/v_F)$, where ρ_a is the "atomic density," $\rho_a\sim e/a^3$, $v_D=j_0/en$ is the drift velocity of the carriers. At $|z|\sim a$ the charge density increases to a value of the order of $\rho_a(a/l)(v_D/v_F)$. Despite the smallness (in the parameter a/l) of the charge density, it is precisely the appearance of the double layer which causes the jump-like increase of the potential φ_ν near the boundary, i.e., the appearance of the resistance (a plot of the potential $\varphi_\nu(z)$ is shown in Fig. 2). We note in conclusion that diffusion scattering of the electrons is apparently always realized in the case of boundaries with large disorientation angles, since the resultant roughnesses are comparable in scale with the de Broglie wavelength of the electron.

3. GRAIN-BOUNDARY RESISTANCE IN SPECULAR SCATTERING

The general method of determining the boundary resistance is based in this case, as before, on a solution of the system (21), (22). However, to find the func-

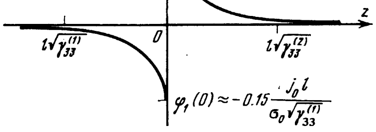

FIG. 2.

tions $A_1(\mathbf{p})$ and $A_2(\mathbf{p})$ it is necessary to understand in detail what is meant by specular scattering of an electron by a grain boundary. The approach to the solution of this question is developed in the paper by Kaganov and Fiks.[3]

The "specularity" of the process of the collision of the electron with the boundary means that the energy and the the x and y components of the momentum are conserved in the course of this collision. The use of this fact makes it possible, given the momentum of the electron incident on the boundary, to obtain the momenta of the reflected and refracted electrons. The corresponding construction is shown in Fig. 1. The fact that only three rather than four waves coexist on the boundary is a consequence of the radiation principle, namely in the refracted wave the z component of the group velocity should be directed away from the boundary.

To find the wave functions and the flux densities in the reflected and refracted waves we must solve the Schrödinger equation in the first and second media, subject to the boundary conditions that the wave function and the probability flux density be continuous on the boundary. The usual procedure can then be used to calculate the reflection and transmission coefficients R and T:

$$R=\left|\frac{v_1-v_2}{v_1+v_2}\right|^2, \quad T=1-R. \tag{36}$$

The quantities v_1 and v_2 are the group velocities in the incident and refracted waves, respectively. They are calculated from the given p_x, p_y, and p_F (which are the same for both media because of the specularity) with the aid of the relations (27). If the point (p_x, p_y) is located outside the region Σ_0 in which the ellipses Σ_1 and Σ_2 are superimposed (see Fig. 3), then the reflection coefficient R becomes equal to unity and the transmission coefficient T becomes equal to zero. This means that the total internal reflection takes place for these electrons. Formally, one of the velocities becomes pure imaginary in this case.

It follows from (23) that the difference between the velocities v_1 and v_2 is due to the difference between the components of the dimensionless tensor of the reciprocal effective mass γ_{ik}, i.e., to the disorientation of the contiguous grains. In the absence of disorientation, and also in the presence of a twin boundary and a symmetric tilt boundary we have v_1 and v_2 and $R=0$, $T=0$, i.e., complete passage takes place and the resistance should vanish.

Using the solution of the quantum-mechanical problem of the elementary act of collision of the electron with the boundary, we can write down the boundary conditions for the considered kinetic problem. These conditions must be formulated in a manner to satisfy the law of conservation of the number of particles passing through the boundary. Simple considerations connected with a calculation of the total probability of the compound event leads to the following boundary conditions for the increments to the distribution function:

$$\begin{aligned}\psi_2^+(0, \mathbf{p}_2') &= R\psi_2^-(0, \mathbf{p}_2)+T\psi_1^+(0, \mathbf{p}_1),\\ \psi_1^-(0, \mathbf{p}_1') &= R\psi_1^+(0, \mathbf{p}_1)+T\psi_2^-(0, \mathbf{p}_2).\end{aligned} \tag{37}$$

Indeed, the transition of the electrons into the state $\mathbf{p}_2'$ can take place either from the state $\mathbf{p}_2$ in the same crystallite by reflection with probability R, or from the state $\mathbf{p}_1$ is another crystallite by refraction with probability T. This reasoning proves the validity of the first boundary condition (37). Similar reasoning justifies the second condition (37). In the actual application of the conditions (37), it is important that the incident and reflected electrons have equal z components of the velocity.

Substituting (16) in (37), we obtain the functions $A_1(\mathbf{p})$ and $A_2(\mathbf{p})$:

$$\begin{aligned}A_1(\mathbf{p}) &= -T(\varphi_2(0)-\varphi_1(0))+Rv_1\tau E_1-Tv_2\tau E_2\\ &+R\frac{1}{v_1\tau}\int_{-\infty}^{0}\varphi_1(z')\exp\left(\frac{z'}{v_1\tau}\right)dz'+T\frac{1}{v_2\tau}\int_{0}^{\infty}\varphi_2(z')\exp\left(-\frac{z'}{v_2\tau}\right)dz',\\ A_2(\mathbf{p}) &= T(\varphi_2(0)-\varphi_1(0))-Rv_2\tau E_2+Tv_1\tau E_1+\\ &+R\frac{1}{v_2\tau}\int_{0}^{\infty}\varphi_2(z')\exp\left(-\frac{z'}{v_2\tau}\right)dz'+T\frac{1}{v_1\tau}\int_{-\infty}^{0}\varphi_1(z')\exp\left(\frac{z'}{v_1\tau}\right)dz'.\end{aligned} \tag{38}$$

Substitution of expressions (38) in formulas (18) and (19) shows, in particular, that the z component of the current density is continuous on going through the boundary:

$$\begin{aligned}j_z(+0)=j_z(-0)=\frac{2e^2}{(2\pi\hbar)^3}\iint_{\Sigma_0}dp_x\,dp_y T\Big[&\varphi_2(0)-\varphi_1(0)\\ &+\frac{1}{v_1\tau}\int_{-\infty}^{0}\varphi_1(z')\exp\left(\frac{z'}{v_1\tau}\right)dz'\\ &-\frac{1}{v_2\tau}\int_{0}^{\infty}\varphi_2(z')\exp\left(-\frac{z'}{v_2\tau}\right)dz'+v_1\tau E_1+v_2\tau E_2\Big],\end{aligned} \tag{39}$$

which confirms once more the correctness of the boundary conditions (37).

Knowledge of the functions $A_2(\mathbf{p})$ and $A_1(\mathbf{p})$ makes it possible to write down the system (21) and (22) as applied to the case of specular scattering:

$$\begin{aligned}\iint_{\Sigma_1}dp_x\,dp_y\Big\{\frac{e^{z/v_1\tau}}{v_1\tau}\Big[&T(\varphi_2(0)-\varphi_1(0))-Rv_1\tau E_1\\ &+Tv_2\tau E_2-R\frac{1}{v_1\tau}\int_{-\infty}^{0}\varphi_1(z')\exp\left(\frac{z'}{v_1\tau}\right)dz'\\ &-T\frac{1}{v_2\tau}\int_{0}^{\infty}\varphi_2(z')\exp\left(-\frac{z'}{v_2\tau}\right)dz'\Big]-E_1\exp\left(\frac{z}{v_1\tau}\right)+\frac{2}{v_1\tau}\varphi_1(z)\\ &-\frac{1}{(v_1\tau)^2}\int_{-\infty}^{0}\varphi_1(z')\exp\left(-\frac{|z-z'|}{v_1\tau}\right)dz'\Big\}=0, \qquad z<0;\end{aligned} \tag{40}$$

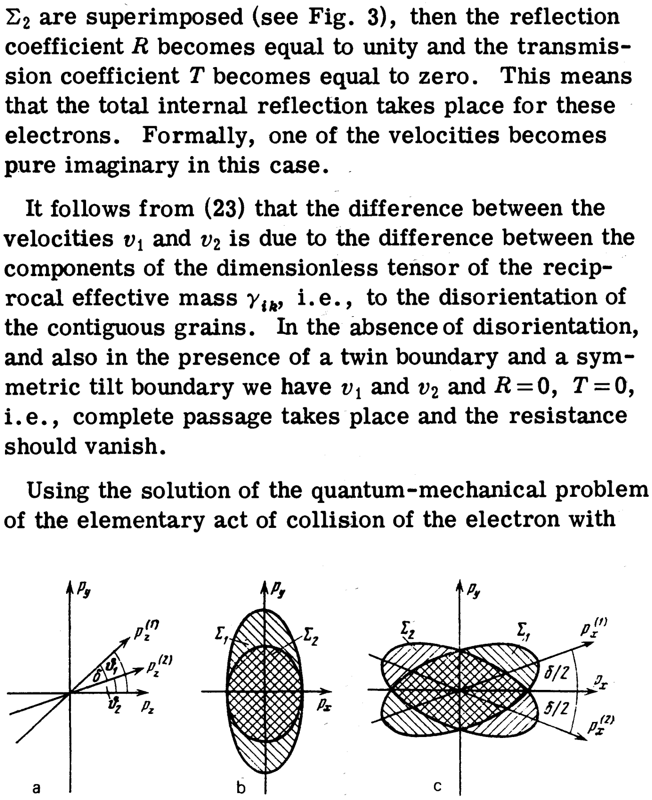

FIG. 3.

$$\iint_{\Sigma_2} dp_x\,dp_y\left\{\frac{e^{-z/v_2\tau}}{v_2\tau}\Big[-T(\varphi_2(0)-\varphi_1(0))+Rv_2\tau E_2\right.$$
$$-Tv_1\tau E_1-R\frac{1}{v_2\tau}\int_0^\infty\varphi_2(z')\exp\left(-\frac{z'}{v_2\tau}\right)dz'$$
$$-T\frac{1}{v_1\tau}\int_{-\infty}^{0}\varphi_1(z')\exp\left(\frac{z'}{v_1\tau}\right)dz'\Big]+E_2\exp\left(\frac{-z}{v_2\tau}\right)+\frac{2}{v_2\tau}\varphi_2(z)$$
$$\left.-\frac{1}{(v_2\tau)^2}\int_0^\infty\varphi_2(z')\exp\left(-\frac{|z-z'|}{v_2\tau}\right)dz'\right\}=0,\qquad z>0. \tag{41}$$

In contrast to the case of diffuse scattering, the system (40) and (41) does not break up into two independent equations. In addition, the structure of the equations of this system is much more complicated because of the presence of the coefficients R and T, which are analytic in v_1 and v_2. As a result of these circumstances, in the general case, at an arbitrary disorientation of the crystallites, it is impossible to find the solutions of (40) and (41) in closed form, and hence to find the resistance of the boundary. However this need not be done, since principal interest attaches to small disorientation of the grains. In fact, at large disorientation angles δ, the scattering, as already mentioned, becomes diffuse and the reasoning of the preceding section applies to this case. At small δ we obtain the resistance, bypassing the solution of (40) and (41), with the aid of the following considerations.

If there is no disorientation ($\delta=0$), then the crystallites are identical, $v_1=v_2$, $E_1=E_2$, $R=0$, $T=1$, the region Σ_1 coincides with Σ_2, the system becomes homogeneous and is satisfied by potentials φ_1 and φ_2 that vanish identically. The resistance of the boundary is in this case, of course, zero. It is perfectly natural to assume that at small δ the potentials φ_1 and φ_2 are small to the extent that the right-hand sides of the system of equations (40) and (41) are small. Therefore at $\delta\ll1$ in all the terms containing φ we can put $v_1=v_2$, $R=0$, and $T=1$, and we can assume that the region Σ_1 coincides with the region Σ_2.

Following this simplification, the integrals over the regions $\Sigma_{1,2}$ in the terms that contain φ can be easily calculated and lead to the appearance, just as in the diffuse case, of integral exponentials. The system is then written in the following form:

$$\varphi_1(s)-\frac{1}{2}\int_{-\infty}^{0}\varphi_1(s')\mathscr{E}_1(|s-s'|)ds'-\frac{1}{2}\int_0^\infty\varphi_2(s')\mathscr{E}_1(s'-s)ds'$$
$$=-\frac{1}{2}(\varphi_2(0)-\varphi_1(0))\mathscr{E}_2(-s)$$
$$+\frac{l}{4\pi p_F^2}\iint_{\Sigma_1}dp_x\,dp_y\left[E_1(1+R)-E_2T\frac{v_2}{v_1}\right]e^{z/v_1\tau},\quad s<0. \tag{42}$$
$$\varphi_2(s)-\frac{1}{2}\int_0^\infty\varphi_2(s')\mathscr{E}_1(|s-s'|)ds'-\frac{1}{2}\int_{-\infty}^{0}\varphi_1(s')\mathscr{E}_1(s-s')ds'$$
$$=\frac{1}{2}(\varphi_2(0)-\varphi_1(0))\mathscr{E}_2(s)$$
$$-\frac{l}{4\pi p_F^2}\iint_{\Sigma_2}dp_x\,dp_y\left[E_2(1+R)-E_1T\frac{v_1}{v_2}\right]e^{-z/v_2\tau},\quad s>0, \tag{43}$$

where $s=z/l\gamma_{33}^{1/2}$ is the dimensionless coordinate introduced previously; in the left-hand sides of (42) and (43) the φ_ν are written for the sake of simplicity as functions of the dimensionless coordinate s. Technically it is convenient to assume that the terms that contain the discontinuity of the potential belong to the right-hand sides of the equations, since the discontinuity itself is a constant subject to determination. The convenience lies in the fact that in this method of analysis the homogeneous system corresponding to expressions (42) and (43) is self-adjoint.

It can be directly verified that this homogeneous system has two solutions: $\varphi_1=\varphi_2=\text{const}$ and $\varphi_1=s$, $\varphi_2=s$. The presence of a solution identically equal to a constant is physically obvious, since the potential is defined accurate to an arbitrary constant. This solution of the homogeneous system holds true both in the diffuse case and for the non-simplified system (40), (41). As to the second solution, it is valid specifically only for small disorientation angles in specular reflections.

For the existence of the solution of our homogeneous system it is necessary to satisfy the condition that the right-hand side be orthogonal to the solution of the corresponding homogeneous system (we take into account in this statement the fact that the system (42), (43) is self-adjoint). It can be verified that the orthogonality of the right-hand side to the first solution (i.e., to a constant) is automatic and takes place not only in the case of small δ, but also for arbitrary δ. On the other hand, orthogonality of the right-hand side to the second solution is a relation from which we obtain the sought discontinuity of the potential (accurate to small quantities of higher order in δ):

$$\int_{-\infty}^{0}\left\{-\frac{1}{2}(\varphi_2(0)-\varphi_2(0))\mathscr{E}_2(-s)+\frac{l}{4\pi p_F^2}\iint_{\Sigma_1}dp_x\,dp_y\left[E_1(1+R)\right.\right.$$
$$\left.\left.-E_2T\frac{v_2}{v_1}\right]e^{z/v_1\tau}\right\}s\,ds+\int_0^\infty\left\{\frac{1}{2}(\varphi_2(0)-\varphi_1(0))\mathscr{E}_2(s)\right.$$
$$\left.-\frac{l}{4\pi p_F^2}\iint_{\Sigma_2}dp_x\,dp_y\left[E_2(1+R)-E_1T\frac{v_1}{v_2}\right]e^{-z/v_2\tau}\right\}s\,ds=0. \tag{44}$$

If we now integrate with respect to s, express the electric fields E_1 and E_2 in terms of j_0 and σ_0 in accord with (10), and divide Eq. (44) by j_0, then we obtain the following expression for the resistance:

$$\mathscr{R}=\frac{3l}{4\pi\sigma_0p_F^2v_F^2\gamma_{33}}\left\{\iint_{\Sigma_1}dp_x\,dp_y\left[(1+R)\frac{v_1^2}{\gamma_{33}^{(1)}}-(1-R)\frac{v_1v_2}{\gamma_{33}^{(2)}}\right]\right.$$
$$\left.+\iint_{\Sigma_2}dp_x\,dp_y\left[(1+R)\frac{v_2^2}{\gamma_{33}^{(2)}}-(1-R)\frac{v_1v_2}{\gamma_{33}^{(1)}}\right]\right\}. \tag{45}$$

Here and below we shall assume $\gamma_{ik}^{(1)}=\gamma_{ik}^{(2)}=\gamma_{ik}$ wherever this assumption does not affect the final results. We calculate the resistance of the tilt and twist boundaries, assuming for simplicity that the Fermi surface is an ellipsoid of revolution.

A. A tilt boundary is characterized by the fact that the principal axes $p_z^{(1)}$ and $p_z^{(2)}$ of the equal-energy ellipsoids are differently oriented relative to the plane of the boundary (see Fig. 3a, the p_z axis is directed along the normal to the plane of the boundary). The matrix $\|\gamma_{ik}\|$ for the first and second ellipsoids takes the form

$$\| \gamma_{ik}^{(\nu)} \| = \begin{pmatrix} \gamma^{-1/2} & 0 & 0 \\ 0 & \gamma^{-1/2}\cos^2\vartheta_\nu + \gamma\sin^2\vartheta_\nu & (\gamma^{-1/2}-\gamma)\sin\vartheta_\nu\cos\vartheta_\nu \\ 0 & (\gamma^{-1/2}-\gamma)\sin\vartheta_\nu\cos\vartheta_\nu & \gamma^{-1/2}\sin^2\vartheta_\nu + \gamma\cos^2\vartheta_\nu \end{pmatrix}. \tag{46}$$

Here $\gamma \equiv \gamma_{33}$ is an element of the matrix $\|\gamma_{ik}\|$ in terms of the principal axes of the ellipsoid ($\det\|\gamma_{ik}\| = 1$). We assume for the sake of argument that $\gamma < 1$ and that the projection of the second ellipsoid on the plane of the boundary lies inside the projection of the first ellipsoid on the same plane, i.e., $\Sigma_2 \subset \Sigma_1$ (see Fig. 3b) In this case the dependence of the z component of the velocity on the z and y components of the momentum takes according to (27) and (46) the form $v_\nu = \gamma_{33}^{(\nu)})^{1/2} v_F l l_\nu$, where

$$u_1 = [1 - n_x^2 - (1-\alpha) n_y^2]^{1/2}, \quad u_2 = [1 - n_x^2 - n_y^2]^{1/2}. \tag{47}$$

Here $n_x = (\gamma^{1/4} p_x)/p_F$, $n_y = [\gamma^{-1/4} (\gamma_{33}^{(2)})^{1/2} p_y]/p_F$, and α is a dimensionless parameter that characterizes the degree of orientation of the crystallites and is small to the extent that the disorientation angle $\delta \equiv |\vartheta_1 - \vartheta_2|$ is small:

$$\alpha \equiv \frac{|\gamma_{33}^{(1)} - \gamma_{33}^{(2)}|}{\gamma_{33}^{(1)}} \approx (\delta\sin 2\vartheta_2 + \delta^2\cos 2\vartheta_2)\frac{\gamma^{-1/2} - \gamma}{\gamma_{33}^{(1)}}. \tag{48}$$

Expression (45) for $\mathscr{R}$, accurate to quantities of higher order of smallness in α, takes the form

$$\mathscr{R} = \frac{3l\gamma_{33}^{1/2}}{4\pi\sigma_0}\left\{ \iint\limits_{\Sigma_0} dn_x\, dn_y \left[R\left(\frac{u_1}{\sqrt{\gamma_{33}^{(1)}}} + \frac{u_2}{\sqrt{\gamma_{33}^{(2)}}}\right)^2 + \left(\frac{u_1}{\sqrt{\gamma_{33}^{(1)}}} - \frac{u_2}{\sqrt{\gamma_{33}^{(2)}}}\right)^2 \right] + \frac{2}{\gamma_{33}^{(1)}} \iint\limits_{\Sigma_1 - \Sigma_0} dn_x\, dn_y\, u_1^2 \right\}, \tag{49}$$

where $\Gamma_0 \equiv \Sigma_1 \cap \Sigma_2 = \Sigma_2$. The calculations yield the resistance of the tilt boundary:

$$\mathscr{R} = \frac{3l\gamma_{33}^{1/2}}{2\pi\sigma_0} \iint\limits_{\Sigma_0} dn_x\, dn_y \left(\frac{u_1}{\sqrt{\gamma_{33}^{(1)}}} - \frac{u_2}{\sqrt{\gamma_{33}^{(2)}}}\right)^2 + O(\alpha^2) = -\frac{9l}{64\sigma_0\gamma_{33}^{1/2}}\alpha^2\ln\alpha + O(\alpha^2). \tag{50}$$

B. In the case of a twist boundary, the principal axes $p_x^{(1)}$ and $p_x^{(2)}$ of the equal-energy ellipsoids are located in the boundary plane symmetrically relative to the p_x direction, and the p_z axis is chosen as before along the normal to the plane of the boundary (see Fig. 3c). The matrix $\|\gamma_{ik}\|$ for the first and second ellipsoids is of the form

$$\| \gamma_{ik}^{(\nu)} \| = \begin{pmatrix} \gamma\cos^2\frac{\delta}{2} + \gamma^{-1/2}\sin^2\frac{\delta}{2} & (-1)^{\nu+1}(\gamma^{-1/2}-\gamma)\sin\frac{\delta}{2}\cos\frac{\delta}{2} & 0 \\ (-1)^{\nu+1}(\gamma^{-1/2}-\gamma)\sin\frac{\delta}{2}\cos\frac{\delta}{2} & \gamma\sin^2\frac{\delta}{2} + \gamma^{-1/2}\cos^2\frac{\delta}{2} & 0 \\ 0 & 0 & \gamma^{-1/2} \end{pmatrix}. \tag{51}$$

Here $\gamma \equiv \gamma_{11}$ is the element of the matrix $\|\gamma_{ik}\|$ in terms of the principal axes of the equal-energy ellipsoid ($\gamma < 1$). The projections of the first and second ellipsoids onto the plane of the boundary ($z = 0$) are oriented symmetrical relative to the p_x direction. The dependence of the z components of the velocity on the x and y components of the momentum takes according to (27) and (51) in the form $v_\nu = (\gamma_{33}^{1/2}) v_F l u_\nu$, where

$$u_\nu = [1 - n_x^2 + (-1)^\nu 2\alpha n_x n_y - n_y^2]^{1/2}. \tag{52}$$

Here $n_x = p_x/\gamma_{11}^{1/2} p_F$, $n_y = p_y/\gamma_{22}^{1/2} p_F$, and α is the small parameter of disorientation of the ellipsoids:

$$\alpha = \frac{|\gamma_{12}|}{(\gamma_{11}\gamma_{22})^{1/2}} = \frac{|\gamma^{-1/2} - \gamma|\sin\delta}{2(\gamma_{11}\gamma_{22})^{1/2}}, \tag{53}$$

where $\delta = |\vartheta_1 - \vartheta_2|$. Expression (45) for $\mathscr{R}$ takes the form

$$\mathscr{R} = \frac{3l}{4\pi\sigma_0\gamma_{33}^{1/2}}\left\{ \iint\limits_{\Sigma_0} dn_x\, dn_y [\mathscr{R}(u_1 + u_2)^2 + (u_1 - u_2)^2] + 2\iint\limits_{\Sigma_1 - \Sigma_0} dn_x\, dn_y\, u_1^2 + 2\iint\limits_{\Sigma_2 - \Sigma_0} dn_x\, dn_y\, u_2^2 \right\}, \tag{54}$$

where $\Sigma_0 \equiv \Sigma_1 \cap \Sigma_2$. The calculations yield the expression

$$\mathscr{R} = \frac{3l}{2\pi\sigma_0\gamma_{33}^{1/2}} \iint\limits_{\Sigma_0} dn_x\, dn_y (u_1 - u_2)^2 + O(\alpha^2) = -\frac{3l}{4\sigma_0\sqrt{\gamma_{33}}}\alpha^2\ln\alpha + O(\alpha^2). \tag{55}$$

Just as in the case of diffuse scattering, the resistance of the grain boundary does not depend on the mean free path l of the electrons in the interior of the metal. However, the dependence of the resistance $\mathscr{R}$ on the disorientation of the crystallites, characterized by the angle δ, is quite substantial and leads to vanishing of the resistance effect at small δ($\propto \delta^2\ln(1/\delta)$). From (48) and (50) it is seen that in the case of a tilt boundary, at certain special orientations of one of the crystallites ($\vartheta = 0$ or $\vartheta = \pi/2$), the resistance $\mathscr{R}$ decreases compared with the value of $\mathscr{R}$ in the case of nonspecial orientations by a factor δ^2. We note also that the results for the resistance (50) and (55) are valid, according to (48) and (53) although for large-angle grain boundaries under the condition that the shape of the Fermi surface differs little from a sphere, i.e., $|\gamma_{11} - \gamma_{33}| \ll 1$. The electric field near the crystallite boundary, in contrast to the diffuse case, remains finite. The case of specular scattering of the electrons by the boundary between single crystals is characterized also by the appearance of a new spatial scale $l^* = \alpha^{1/2} l$ of the variation of the potential. Just as in the diffuse case, the physical cause of the resistance of the boundary is the appearance of a double layer, whose "thickness" is determined by the orientational parameters of the bicrystal. At angles $\delta \sim 1$ the "specular" resistance is of the same order as the diffuse resistance, i.e., the resistance of the polycrystal takes in this case the form

$$\rho = \rho_0(1 + \beta l/d),$$

where ρ_0 is the resistivity of the single crystal and the parameter $\beta \sim 1$ depends on the distribution of the grain orientations.

The determination of the character of the dependence of the resistance on the crystallite disorientation angle [$\mathscr{R} \propto \delta^2\ln(1/\delta)$] allows us to state that if we introduce the diffuseness coefficient in the grain-boundary problem, then this coefficient turns out to be proportional to $^2\ln(1/\ )$ at small crystallite disorientation angles $\delta^2\ln(1/\delta)$.

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[1] To avoid possible misunderstandings, we note that the total potential $\Phi_\nu(z)$ is constructed in accordance with (13) using the formula $\Phi_\nu(z) = -E_\nu z + \varphi_\nu(z) - \varphi_\nu(0)$, so that it is continuous on the boundary.

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Dielectric constants of solid electrolytes and transition to superionic state

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A mechanism whereby an ionic conductor goes into the superionic state is proposed. The disordering of the cation sublattices, which consists of a shift of a cation from a site to one of the interstices of the same unit cell, if the number of the interstices is large, leads to an increase of the dielectric constant ε of the crystal, since dipoles consisting of interstitial and site cations are produced in the system in this case. On the other hand, the shift of cations from sites to interstices with increasing ε consumes less energy, because of the larger polarization of the medium by the dipole. As a result, with increasing T, a first-order phase transition from a state with low ε (ordered cation sublattice) into a state with high ε (disordered cation sublattice) can occur. At large ε, conditions become easier also for the production of carriers, i.e., of excess cations in other unit cells and of the vacancies that remain after their departure, since the Coulomb interaction between them becomes weaker. The jump of ε leads therefore to a jump in the conductivity.

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It is customary to single out from among the solid electrolytes the group of superionic conductors, which have relatively high ionic conductivity ($\sigma > 10^{-3}\Omega^{-1}\,\mathrm{cm}^{-1}$) above a certain temperature.[1] As a rule, the transition to the high-conductivity state proceeeds jumpwise, with the resistance changing by several orders of magnitude. This jump differs substantially from the insulator-metal phase transition in electronic conductors in that the resistance in the high-conductivity phase, just as in the low-conductivity phase, depends exponentially on the temperature, but the activation energy in the former is much lower than in the latter. A transition into the superionic state is accompanied simultaneously by partial disordering of the lattice, wherein the translational symmetry is lost in the arrangement of the cations that carry the current, but is preserved for the low-mobility anions (it is customary to speak of melting of the cation sublattice and preservation of the anion sublattice).

A characteristic feature of materials that can become superionic is the complexity of their crystallographic structure. The latter manifests itself, in particular, in the large number of equivalent unit-cell interstices to which a cation can go from its normal stable position. It must therefore be emphasized that, despite the prevailing opinion, the very melting of the cation sublattice still does not automatically lead to high conductivity. In fact, the charge transfer consists of a transition of cations from some unit cells to others, i.e., its necessary condition is the presence of "polar states"—unit cells with either excess or deficit of cations. Yet the loss of translational symmetry of the cations can take place also without the cations going from cell to cell—simply by the cation going into one of the interstices within the same unit cell. This kind of "melting" is similar in essence to the "order-disorder" phase transition in ferroelectrics which, as is well known, is usually not accompanied by high conductivity. The reason is that in typical ferroelectrics the energy needed to produce the excess cations and their vacancies is high. It can be lower in solid electrolytes, but certainly exceeds the energy needed by the cation to leave a site and go to an interstice in the same unit cell.

At the same time, the physics of the melting of the cation sublattice in solid electrolytes is not clear (it differs from the disorder in ferroelectrics in that in the latter the cations become redistributed among equivalent positions within the unit cell, whereas in solid electrolytes the moves are from sites to interstices). In the previously advanced theories[2,3] it is postulated that attraction exists between the cations in the interstices, so that when the number of cations increases formation of more remote defects of this type is facilitated and a first-order phase transition into a state with a molten cation sublattice becomes possible. The physical nature of the attraction, and whether it exists at all, remains unclear. It is therefore desirable to construct a theory of superionic conductors without using yet-unfounded hypotheses. The present paper is an attempt to construct such a theory. We emphasize that the mechanism proposed below for the

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