P. J. Price

Anisotropic Conduction in Solids Near Surfaces

Abstract: A reduction in the electrical conductivity of a solid results from "diffuse" reflection of electrons from the surfaces. The effect occurs for specular reflection also, if the operative electron-energy surfaces are not spherical. A theory of the latter case is given here. The average conductivity of a thin crystal tends to a finite limit (rather than zero) as the thickness tends to zero. The Hall effect for the same circumstances is also treated.

1. Introduction

It is well known that the electrons near a surface contribute less than the average electron to the electrical conductivity of a solid if they are diffusely, rather than specularly, reflected by the surface. For the "isotropic" model (spherical surfaces of constant energy, spherically symmetrical bulk scattering), and completely diffuse reflection (expectation of electron velocity after a reflection equal to zero), the theory of this effect has been extensively developed.[1,2,3] The present paper concerns the generalization of the theory, for conduction by a thin single-crystal plate with parallel sides, to nonspherical electron energy surfaces. Two new features of the phenomenon appear with this generalization:

(a) The conductivity is not in general isotropic, with respect to different directions parallel to the two bounding surfaces, even for a cubic crystal.

(b) Even purely specular reflection is in general associated with a change in the conductivity.

These two features are examined below by working out the theory with specular reflection for the standard case of a band-edge neighborhood with ellipsoidal energy surfaces. We shall be concerned only with situations where the thickness of the crystal, a, is large compared with the lattice constant, so that the electron state may be specified by a position vector $\mathbf{r}$ and a crystal momentum vector $\mathbf{p}$ (together with spin state and band index), and where the electronic state when a current is flowing may be adequately determined by a Boltzmann equation for the distribution function $f(\mathbf{p}, \mathbf{r})$.

The problem has previously and independently been treated by Ham and Mattis,[4] especially the diffuse reflection case. The idea presented in Section 2 below (that the normal component of the *wavevector* changes in specular reflection, by an amount given by energy conservation) was first introduced by them.[4] The mathematical technique used here is different, however. The "vector mean free path" concept,[5,6] generalized to allow for the surface reflections, is used to calculate the components of the conductance of a thin crystal without first solving for $f(\mathbf{p}, \mathbf{r})$. A principal result, eqs. (35), (37), was previously obtained by Ham.[7]

2. Specular reflection

An essential preliminary is to determine the relation between electron states before and after a specular reflection from the boundary surface. It is supposed here that *the direction of the change in crystal momentum on reflection is normal to the surface.* This principle may be made plausible by two (idealized) examples:

(a) The surface acts on the electron by a potential whose gradient is normal to the surface and very small in magnitude (so that the surface region is wide compared with a lattice constant but narrow compared with a "bulk mean free path"). Then the electron trajectory is given by

$$d\mathbf{p}/dt = e \text{ grad (surface potential)},$$

and hence the total change in $\mathbf{p}$ is normal to the surface.

(b) The crystal terminates abruptly at an atomic plane. If the electron wavefunction is expressed as a linear combination of the band Wannier functions,

$$\psi(\mathbf{r}) = \Sigma_n A_n \alpha(\mathbf{r} - \mathbf{R}_n),$$

then the effect of the surface may be given by the condition that A_n vanishes at the boundary sheet of lattice cells. Since for a Bloch wave $A_n = \exp(i\,\mathbf{p}\cdot\mathbf{R}_n/\hbar)$, it follows again that the component of $\mathbf{p}$ parallel to the surface must be the same for incident and reflected waves.

A further condition which must be satisfied is, of course, that the electron energy ε is the same for the

initial and final states. Thus, if $\mathbf{p}'$ refers to the final, $\mathbf{p}$ to the initial, state, we have

$$\mathbf{p}'-\mathbf{p}=p_i\mathbf{k}\,, \tag{1}$$

$$\varepsilon(\mathbf{p}')-\varepsilon(\mathbf{p})=0\,, \tag{2}$$

where $\mathbf{k}$ is the unit vector normal to the surface. These conditions correspond to the "construction" shown in Fig. 1. The full line represents a section, in a plane containing $\mathbf{k}$, of a surface of constant energy in $\mathbf{p}$-space, and the points P, P′ represent the initial and final states.

Obviously, conditions (1) and (2) do not necessarily determine the final state uniquely. In the conduction band of germanium, for example, inter-valley, as well as intra-valley, reflections may satisfy them. There is no obvious general way to settle this question, and so it is natural to tentatively assume at first, in applications, that only intra-valley reflections occur. (One may be able to choose orientations, for measurement, such that only intra-valley reflections are possible. For example, by making the normal to the surface a [1, 1, 1] direction for *n*-germanium, or—presumably—the triad axis for bismuth. For metals, one should by a suitable choice of orientation be able to eliminate *umklapp* reflections, leaving only a physically unique $\mathbf{p}'$ for each $\mathbf{p}$.)

An "ellipsoidal" band-edge neighborhood has a constant inverse mass tensor $\boldsymbol{\gamma}$. The electron energy is

$$\varepsilon=\tfrac{1}{2}\mathbf{p}\cdot\boldsymbol{\gamma}\cdot\mathbf{p}\,, \tag{3}$$

and the electron velocity is

$$\mathbf{v}=\partial\varepsilon/\partial\mathbf{p}=\boldsymbol{\gamma}\cdot\mathbf{p}\,. \tag{4}$$

Then

$$2(\varepsilon'-\varepsilon)=(\mathbf{p}'-\mathbf{p})\cdot(\mathbf{v}'+\mathbf{v})\,. \tag{5}$$

It follows from eqs. (1), (2) and (5) that the component of *velocity* normal to the surface is reversed in specular reflection, for the present case. However, the component of $\mathbf{v}$ parallel to the surface also changes in general. In terms of Cartesian coordinates with the Z-axis normal to the surface (which will be used throughout this paper), we have

$$p_z'-p_z=-2v_z/\gamma_{zz}$$

and hence

$$\left.\begin{aligned} v_x'-v_x&=-2(\gamma_{xz}/\gamma_{zz})v_z\,,\\ v_y'-v_y&=-2(\gamma_{yz}/\gamma_{zz})v_z\,,\end{aligned}\right\} \tag{6}$$

in addition to the above result

$$v_z'=-v_z\,. \tag{7}$$

3. Conduction with specular reflection

At a point far away from boundaries in a homogeneous crystal, when Boltzmann's equation is valid as stated in Section 1, the electronic conductivity tensor is[5,6]

$$\boldsymbol{\sigma}=(e^2/h^3kT)If_0(1-f_0)\mathbf{lv}\,, \tag{8}$$

where I stands for integration $\int d^3\mathbf{p}$ - - - - over the Brillouin zone and summation over bands and spin orientations, $f_0(\varepsilon)$ is the Fermi distribution function, and the "vector mean free path" $\mathbf{l}$ is given by[6]

$$\mathbf{l}=\int_0^\infty \mathbf{v}|t)\,dt\,. \tag{9}$$

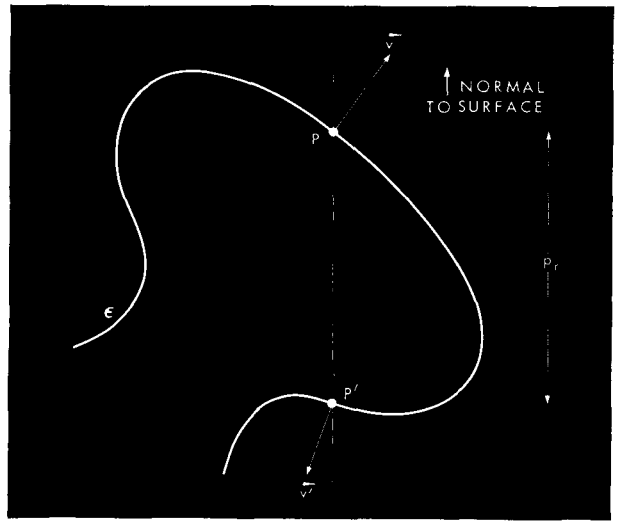
Here $\mathbf{v}|t)$ stands for the expectation of the velocity $\mathbf{v}$ of an electron after an interval t since it was in a definite specified state (of which $\mathbf{l}$ is then a function).

The foregoing definition (9) of $\mathbf{l}$ may be generalized, for present purposes, simply by including the surface reflections in the electron "histories" (of the ensemble which is averaged over in the definition of $\mathbf{v}|t)$). (See also Section 2.5 of Reference 2.) The result is then a function of position $\mathbf{r}$ as well as of electronic (Bloch) state. The local current density, for a given electric field, is *not* in general given by the local value of $If_0(1-f_0)\mathbf{l}(\mathbf{r})\mathbf{v}$; but the volume average, $(1/V)\int d^3\mathbf{r}\boldsymbol{\sigma}(\mathbf{r})$, of the conductivity *is* equal to the right-hand side of (8) with the volume average of the new $\mathbf{l}$ substituted.[8] It will be convenient to use a single symbol, A, for the operator $(1/V)\int d^3\mathbf{r}$ - - - - . Then

$$A\boldsymbol{\sigma}=(e^2/h^3kT)If_0(1-f_0)(A\mathbf{l})\mathbf{v}\,. \tag{10}$$

We wish to calculate the components of $A\boldsymbol{\sigma}$ in the XY plane, for the geometry shown in Fig. 2. An electron starting from point O, in the state represented by P in Fig. 1, follows the path OR_1R_2 - - - alternating between states represented by P and P′, until it is scattered inside the crystal. We shall assume that the expectation of $\mathbf{v}$ after this "bulk" scattering is zero. If it were not for the reflections, the vector mean free path would therefore be equal to $\tau\mathbf{v}$, where $1/\tau$ is the scattering frequency. The probability that the electron is scattered after an interval $\geqslant t_1$, out of the initial state, is of course $\exp(-t_1/\tau)$.

Figure 1 **Construction for specular reflection.**



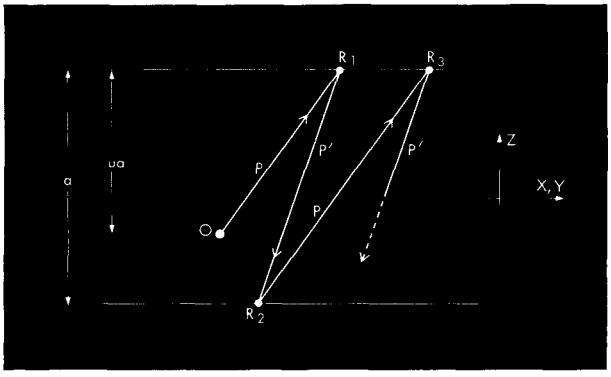


Figure 2 **Electron path with specular reflections.**

By summing over the segments of path OR_1, R_1R_2, - - - - - and allowing for the decreasing probabilities of tracing successive segments still unscattered, we find

$$\mathbf{I}=\tau\mathbf{v}+(\tau'\mathbf{v}'-\tau\mathbf{v})e^{-u\phi}\,\frac{(1-e^{-\phi'})}{1-e^{-(\phi+\phi')}} \tag{11}$$

(and similarly for any other state variable replacing $\mathbf{v}$ in (9)), where

$$\phi\equiv a/\tau|v_z|\,, \tag{12}$$

ua is the perpendicular distance from the initial position of the electron to the surface towards which the z component of $\mathbf{v}$ is directed (see Fig. 2), and the primes refer to the state after the first reflection at R_1. The averaging A reduces to $(1/a)\int dz$ - - -, the integral being taken over the thickness of the plate: that is, to $\int_0^1 du$ - - - - -. Then

$$A\mathbf{I}=\tau\mathbf{v}+(\tau'\mathbf{v}'-\tau\mathbf{v})\left[\frac{1}{\phi}\cdot\frac{(1-e^{-\phi})(1-e^{-\phi'})}{1-e^{-(\phi+\phi')}}\right]. \tag{13}$$

We now specialize to the "ellipsoid" case given by eqs. (3) to (7), and also assume that τ is a function of energy ε only. Then $\tau'=\tau$, $\phi'=\phi$, and the factor [ ] of (13) becomes

$$[\quad]=\psi(\phi)\equiv\frac{1}{\phi}\left(\frac{1-e^{-\phi}}{1+e^{-\phi}}\right). \tag{14}$$

It is convenient to factor out of the operation I, in (10), the following average over a surface of constant energy ($\varepsilon=\varepsilon_1$, say) for any function g of electron state:

$$\bar{g}\equiv I[g\delta(\varepsilon-\varepsilon_1)]/I\delta(\varepsilon-\varepsilon_1)=\bar{g}(\varepsilon_1)\,.$$

(Then $Ig=\int\bar{g}(\varepsilon)N(\varepsilon)d\varepsilon$ where $N(\varepsilon_1)$ is the density of states $I\delta(\varepsilon-\varepsilon_1)$.) By (6), (13) and (14),

$$A\overline{l_pv_q}=\tau\overline{v_pv_q}-2\tau(\gamma_{pz}/\gamma_{zz})\overline{v_zv_q\psi}\,, \tag{15}$$

where $p, q=x, y$. The first term of (15) corresponds to the ordinary bulk conductivity, and is given by

$$\overline{\mathbf{vv}}=\tfrac{2}{3}\varepsilon\boldsymbol{\gamma}\,.$$

The second term is obtained similarly, in the limit of very small thickness a. Since

$$\left.\begin{aligned}&\psi\to\tfrac{1}{2}, && \phi\to 0\,;\\ &\psi\approx 1/\phi=\tau|v_z|/a, && \phi\to\infty\,,\end{aligned}\right\} \tag{16}$$

we may in this limit replace ψ by $\frac{1}{2}$ in (15) (neglecting the deviation from this value over the small part of the energy surface where $|v_z|$ is not $\gg a/\tau$). Then

$$A\overline{l_pv_q}=\tau\tfrac{2}{3}\varepsilon(\gamma_{pq}-\gamma_{pz}\gamma_{qz}/\gamma_{zz})\,. \tag{17}$$

Thus $A\sigma_{pq}$ differs from the "bulk" value of σ_{pq} by a factor $(1-\gamma_{pz}\gamma_{qz}/\gamma_{pq}\gamma_{zz})$. Since this factor depends on p, q, in general the effective conductivity is anisotropic even for a combination of "ellipsoidal" band-edge neighborhoods with cubic over-all symmetry.

The fact that for pure specular reflection the average conductivity differs from the bulk value, and tends to a smaller but *finite* limit at zero thickness, may be understood as follows: The disturbance of the distribution function caused by an electric field is proportional (i.e., on a given energy surface) to $\mathbf{E}\cdot\mathbf{v}$, and the current due to this disturbance is proportional to $\mathbf{I}$; so the conductivity contributed by a given energy shell is proportional to $\overline{\mathbf{Iv}}$. For the bulk, with $\mathbf{I}=\tau(\varepsilon)\mathbf{v}$, it is hence proportional to $\overline{\mathbf{vv}}$. For the limit of small thickness, many links in the path $OR_1R_2R_3$ - - - (Fig. 2) are covered before the velocity is randomized by a bulk scattering. Since equal times are spent in the states P and P', by (9)

$$\mathbf{I}=\tau(\mathbf{v}+\mathbf{v}')/2\,.$$

The average $\overline{\mathbf{Iv}}$ weights states P and P' equally, but in the two limits there are different correlations between the velocities in the first and second factors. Specifically,

$\frac{1}{2}(\mathbf{vv}+\mathbf{v}'\mathbf{v}')$ (bulk) is replaced by

$$\tfrac{1}{4}(\mathbf{v}+\mathbf{v}')(\mathbf{v}+\mathbf{v}')=\tfrac{1}{2}(\mathbf{vv}+\mathbf{v}'\mathbf{v}')-\tfrac{1}{4}(\mathbf{v}-\mathbf{v}')(\mathbf{v}-\mathbf{v}')\,.$$

This correlation effect is the mathematical origin of the change in conductivity: it is associated with the physical situation, in the thin limit, that a free path mixes states P and P' in proportions asymptotically independent of thickness. In a similar way the Hall constant tends to a finite limiting value as the crystal thickness tends to zero (Section 6).

For greater thicknesses, the generalization of (17) may be expressed in terms of the minimum value of ϕ on the energy surface:

$$\kappa_z\equiv a/\tau\sqrt{(2\gamma_{zz}\varepsilon)}\,. \tag{18}$$

(κ_z is the generalization of the parameter κ of Reference 2.) Let λ be the ratio of v_z to its maximum value, $\sqrt{(2\gamma_{zz}\varepsilon)}$, so that $\phi=\kappa_z/|\lambda|$. Then it follows from the geometry of ellipsoids (see the Appendix) that the required average of $\psi(\phi)$ over an energy surface is

$$\overline{v_zv_q\psi}\,\Big/\,\overline{v_zv_q}=3\int_0^1\psi(\kappa_z/\lambda)\lambda^2d\lambda\,. \tag{19}$$

In the limit of very *large* thickness, by (16) the right-hand side of (19) is equal to $3/4\kappa_z$. In place of (17) we then have

$$A\overline{l_p v_q} = \tau\varepsilon\{\tfrac{2}{3}\gamma_{pq} - (\gamma_{pz}\gamma_{qz}/\gamma_{zz})\tau\sqrt{(2\gamma_{zz}\varepsilon)}/a\}\,. \qquad (20)$$

Obviously, each surface may be regarded as contributing half the difference between $A\sigma_{pq}$ and the bulk value of σ_{pq}, in this limit. If $\tau\sqrt{\varepsilon}$ is independent of ε, and in any case for a metal or degenerate semimetal in the residual resistance range, we may say that each surface adds, to the conductance $aA\sigma_{pq}$ of a square, $(-3\gamma_{pz}\gamma_{qz}/4\gamma_{pq}\gamma_{zz})$ times the "bulk" contribution from a thickness $\tau\sqrt{2\gamma_{zz}\varepsilon}$ of crystal.

For any thickness, we have from (14), (15) and (19):

$$A\overline{l_p v_q} = \tfrac{2}{3}\tau\varepsilon[\gamma_{pq} - G(\tfrac{1}{2}\kappa_z)\gamma_{pz}\gamma_{qz}/\gamma_{zz}]\,, \qquad (21)$$

where

$$G(x) \equiv \frac{3}{x}\int_1^\infty \tanh(xs)\,\frac{ds}{s^5}\,. \qquad (22)$$

4. Diffuse reflection

This case will be briefly discussed here, with the assumption that the x, y components of velocity have zero expectation after a reflection.[9] Then the trajectories contributing to (9) terminate at the first surface reached, if not before. Therefore

$$l_p(\mathbf{r}) = \tau v_p(1 - e^{-ua/\tau|v_z|})\,. \qquad (23)$$

The effective mean free path is hence given by

$$Al_p = \tau v_p\{1 - (1 - e^{-\phi})/\phi\}\,. \qquad (24)$$

For the "ellipsoid" case, $A\overline{l_p v_q}$ is obtained by substituting $\kappa_z/|\lambda|$ for ϕ and averaging $\{\ \}$ of (24) as in Section 3. The calculation in the present case is somewhat more complicated. Using eq. (A7) of the Appendix, we find

$$A\overline{l_p v_q} = \tau\overline{v_p v_q}\,F(\kappa_z, \omega_{pq})\,, \qquad (25)$$

where

$$F(\kappa, \omega) \equiv 1 - \frac{3}{2}\frac{1}{\kappa}\left\{\frac{1+\omega}{4} - \int_1^\infty \left(\frac{1-\omega}{s^3} - \frac{1-3\omega}{s^5}\right)e^{-s\kappa}ds\right\} \qquad (26)$$

and

$$\omega_{pq} \equiv \gamma_{pz}\gamma_{qz}(\boldsymbol{\gamma}^{-1})_{zz}/\gamma_{pq}\,. \qquad (27)$$

The function $F(\kappa, 0)$ is the same as $\kappa/\Phi(\kappa)$ given by eq. (17) of Reference 2. Thus (25) generalizes Fuchs' result for spherical symmetry to "ellipsoidal symmetry." We have

$$F(\kappa, \omega) \approx \tfrac{3}{4}(1-\omega)\kappa\log(1/\kappa), \quad \kappa \to 0\,, \qquad (28)$$

and therefore the result corresponding to (17) in Section 3 is

$$A\overline{l_p v_q} = \tfrac{1}{2}\tau\varepsilon[\gamma_{pq} - \gamma_{pz}\gamma_{qz}(\boldsymbol{\gamma}^{-1})_{zz}]\kappa_z\log(1/\kappa_z)\,. \qquad (29)$$

Also

$$F \approx 1 - \frac{3(1+\omega)}{8\kappa}\,, \quad \kappa \to \infty\,, \qquad (30)$$

and therefore in place of (20) we have

$$A\overline{l_p v_q} = \tau\varepsilon\{\tfrac{2}{3}\gamma_{pq} - \tfrac{1}{4}[\gamma_{pq} + \gamma_{pz}\gamma_{qz}(\boldsymbol{\gamma}^{-1})_{zz}]\tau\sqrt{(2\gamma_{zz}\varepsilon)}/a\}\,. \qquad (31)$$

5. Application

The result (17) is transformed below to a form suitable for some applications. It is recalled that (17) refers to specular intra-valley reflection in a crystal thin compared to the appropriate mean free path, $\tau\sqrt{(2\varepsilon\gamma_{zz})}$, for bulk scattering, and that it was obtained by assuming that bulk scattering is randomizing (expectation of electron velocity after a scattering is zero) and has a frequency, $1/\tau$, which is a function of energy only. We have, for one "valley,"

$$\sigma_{pq}(a \to \infty) = \xi\gamma_{pq}\,, \qquad (32)$$

$$A\sigma_{pq}(a \to 0) = \xi(\gamma_{pq} - \gamma_{pz}\gamma_{qz}/\gamma_{zz})\,, \qquad (33)$$

where ξ is a constant given by (8) and proportional to

$$If_0(1-f_0)\tau\varepsilon/kT\,.$$

We consider the usual case that two of the principal values of $\boldsymbol{\gamma}$ are equal: we denote them by $\gamma_\perp$, and the third by $\gamma_\parallel$. Let the axis of revolution (the third principal axis) make an angle θ with the XY plane, and be perpendicular to the Y axis. Then

$$\left.\begin{aligned} \gamma_{xx} &= \gamma_\parallel c^2 + \gamma_\perp s^2\,,\\ \gamma_{yy} &= \gamma_\perp\,,\\ \gamma_{zz} &= \gamma_\parallel s^2 + \gamma_\perp c^2\,,\\ \gamma_{xz} &= (\gamma_\parallel - \gamma_\perp)sc\,,\\ \gamma_{xy} &= \gamma_{yz} = 0\,, \end{aligned}\right\} \qquad (34)$$

where s and c are respectively $\sin\theta$ and $\cos\theta$. If we write the contribution of this valley to the "surface conductivity" tensor (the x, y components of $A\boldsymbol{\sigma}$) as

$$\sigma_s(a) = \begin{pmatrix} \xi\gamma^s{}_\parallel & 0 \\ 0 & \xi\gamma_\perp \end{pmatrix}, \qquad (35)$$

then

$$\gamma^s{}_\parallel(a \to \infty) = \gamma_\parallel c^2 + \gamma_\perp s^2\,, \qquad (36)$$

$$\gamma^s{}_\parallel(a \to 0) = \frac{\gamma_\parallel\gamma_\perp}{\gamma_\parallel s^2 + \gamma_\perp c^2}\,. \qquad (37)$$

It is recalled that $\gamma_\parallel$ and $\gamma_\perp$ are respectively equal to $1/m_\parallel$ and $1/m_\perp$, in the usual notation. If there is an n-fold axis, with $n>2$, normal to the surface, the surface conductivity will of course be isotropic. A set of equivalent valleys equally inclined to the axis will contribute $\frac{1}{2}\xi(\gamma_\perp + \gamma^s{}_\parallel)$ per valley to the surface conductivity.

It should be noted that, for the conditions resulting in (33),

$$Al_z = 0 \qquad (38)$$

and

$$A\sigma_{pz}=A\sigma_{zp}=A\sigma_{zz}=0\,, \tag{39}$$

$p=x, y$.

6. The Hall effect

For conduction uninfluenced by surfaces, we have[5]

$$\mathbf{J}=\boldsymbol{\sigma}(\mathbf{H})\cdot\mathbf{E}=\boldsymbol{\sigma}(0)\cdot\mathbf{E}-\mathbf{H}\cdot\boldsymbol{\beta}(0)\times\mathbf{E}+0(H^2) \tag{40}$$

where $\boldsymbol{\sigma}(0)$ is given by (8) and $\boldsymbol{\beta}(0)$, the coefficient of the linear Hall effect, is given by

$$\left.\begin{aligned}\beta(0)_{ij}&=(e^3/2ckTh^3)If_0(1-f_0)S_{ij}\,,\\ S_{ij}&\equiv\Sigma_r\Sigma_s\Sigma_t\Sigma_u e_{irs}e_{jtu}v_r(\partial l_t/\partial p_s)l_u\,.\end{aligned}\right\} \tag{41}$$

(The e_{ijk} are the usual "skew triadic" coefficients, zero unless i, j, k are all different and otherwise ±1 according as the order of i, j, k is cyclic or countercyclic.) Just as (10) is related to (8), the average over the width of a thin crystal $A\boldsymbol{\beta}(0)$ is obtained from (41) by again generalizing $\mathbf{l}$ to take into account the surface reflections and scatterings and by then replacing l_tl_u in (41) by $A(l_tl_u)$. For specular reflection with $\tau=\tau(\varepsilon)$ we find

$$\begin{aligned}A(\mathbf{ll})=\tau^2\mathbf{vv}&+\tau^2\psi(\phi)\{\mathbf{v}(\mathbf{v}'-\mathbf{v})\\&+(\mathbf{v}'-\mathbf{v})\mathbf{v}+\tfrac{1}{2}(\mathbf{v}'-\mathbf{v})(\mathbf{v}'-\mathbf{v})\}\,,\end{aligned} \tag{42}$$

where ψ is given by (14). In the limit where the thickness, a, tends to zero, $\psi\to\frac{1}{2}$ and hence

$$A(\mathbf{ll})=(A\mathbf{l})(A\mathbf{l}) \tag{43}$$

where, as in Section 3,

$$A\mathbf{l}=\tau\mathbf{v}+\tfrac{1}{2}\tau(\mathbf{v}'-\mathbf{v})\,. \tag{44}$$

From (6), (43) and (44), for an "ellipsoidal" band-edge neighborhood

$$A\overline{S}_{zz}=\tau^2\,\tfrac{2}{3}\varepsilon(2(\gamma'_{xy})^2-2\gamma'_{xx}\gamma'_{yy})\,, \tag{45}$$

where

$$\gamma'_{pq}\equiv\gamma_{pq}-\gamma_{pz}\gamma_{qz}/\gamma_{zz}\,. \tag{46}$$

For a single valley with rotational symmetry and oriented as in Section 5 it follows that $A\beta(0)_{zz}$ is proportional to $2(\gamma_{xx}-(\gamma_{xz})^2/\gamma_{zz})\gamma_{yy}$, compared to $2\gamma_{xx}\gamma_{yy}$ for the "bulk" limit of large thickness. Therefore, by (34), for a set of equivalent valleys equally inclined to the surface normal,

$$\left.\begin{aligned}\frac{\beta(0)_{zz}(a\to0)}{\beta(0)_{zz}(a\to\infty)}&=\frac{1}{1+\chi}\,,\\ \chi&\equiv\frac{s^2c^2(\gamma_\parallel-\gamma_\perp)^2}{\gamma_\parallel\gamma_\perp}\,.\end{aligned}\right\} \tag{47}$$

In the same limit $a\to0$, for specular reflection, the other components of $\boldsymbol{\beta}(0)$ are zero. Thus it results from the foregoing theory that the linear Hall current — the second term of (40) — has no component normal to the surface. However, $\sigma(0)_{zz}$ vanishes in the same limit and therefore the Hall *field* normal to the surface does not necessarily vanish.

Appendix: Geometry of ellipsoidal energy surfaces

Formulas are developed here for transforming the averages

$$\bar{g}(\varepsilon_1)=\overline{g(\mathbf{p})}\equiv I[g\delta(\varepsilon-\varepsilon_1)]/I\delta(\varepsilon-\varepsilon_1) \tag{A1}$$

over an energy surface (3) into integrals over v_z. The planes of constant v_z intersect the energy surface in ellipses (which we will call "v_z ellipses"). The extreme planes are tangent to the energy surface at

$$p_x=p_y=0\,,\qquad p_z=\pm\sqrt{(2\varepsilon/\gamma_{zz})}\,, \tag{A2}$$

where the maximum and minimum values of v_z are $\pm\sqrt{(2\gamma_{zz}\varepsilon)}$. Since the system of ellipsoids (3) is obtained from the system of spheres $\varepsilon=$ const. p^2 by a linear transformation in $\mathbf{p}$ space, the average $\overline{g(v_z)}$ may be expressed as an integral over v_z with constant weighting factor:

$$\overline{g(v_z)}=\tfrac{1}{2}\int_{-1}^{1}g(v_z)\,d\lambda\,, \tag{A3}$$

where

$$\lambda=v_z/\sqrt{(2\gamma_{zz}\varepsilon)}\,. \tag{A4}$$

The result (19) is obtained by the following argument: The factor v_q (it is recalled that p, q stand for x or y) must be replaced by the appropriate average over each v_z ellipse. The required average is, obviously, proportional to v_z, and therefore the correct substitution in the integral over v_z is

$$v_q\to v_z(\overline{v_qv_z})\,/\,(\overline{v_z^2})\,. \tag{A5}$$

The substitution required for deriving (25) is obtained as follows: we have

$$\begin{aligned}v_pv_q=(&\gamma_{px}\gamma_{qx}p_x^2+\gamma_{px}\gamma_{qy}p_xp_y+\ +\ \ )\\&+(\gamma_{px}\gamma_{qz}p_xp_z+\ +\ +\ \ )\\&+\gamma_{pz}\gamma_{qz}p_z^2\,.\end{aligned} \tag{A6}$$

It is evident from (A2) that the centers of the v_z ellipses are at $p_x=p_y=0$, and therefore that the substitution for the first line of (A6) is proportional to $1-\lambda^2$, that for the second is zero, and the substitution for the third line is proportional to λ^2. Let the required substitutions be $A(1-\lambda^2)$ and $B\lambda^2$. Then

$$\tfrac{2}{3}A+\tfrac{1}{3}B=\overline{v_pv_q}=\tfrac{2}{3}\varepsilon\gamma_{pq}\,,$$

$$\tfrac{1}{3}B=\gamma_{pz}\gamma_{qz}\overline{p_z^2}=\tfrac{2}{3}\varepsilon\gamma_{pz}\gamma_{qz}(\boldsymbol{\gamma}^{-1})_{zz}\,.$$

Hence, finally,

$$v_pv_q\to\frac{3}{2}\,\overline{v_pv_q}[(1-\omega_{pq})-\lambda^2(1-3\omega_{pq})]\,, \tag{A7}$$

where

$$\omega_{pq}\equiv\gamma_{pz}\gamma_{qz}(\boldsymbol{\gamma}^{-1})_{zz}/\gamma_{pq}\,. \tag{A8}$$

(Note that, according to (34), $(\boldsymbol{\gamma}^{-1})_{zz}=\gamma_{xx}/\gamma_\parallel\gamma_\perp$.)

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References and footnotes

1. K. Fuchs, *Proc. Camb. Phil. Soc.* **34,** 100 (1938).
2. E. H. Sondheimer, *Advances in Physics,* **1,** 1 (1952).
3. Conduction in an inversion layer neighboring a semiconductor surface has been discussed by J. R. Schrieffer, *Phys. Rev.* **97,** 641 (1955). The extension to anisotropic conditions (not considered here) is treated in Reference 4.
4. F. S. Ham and D. Mattis, "Electrical Properties of Thin Film Semiconductors," Technical Report No. 4, University of Illinois, 1955. See also the accompanying paper here.
5. P. J. Price, *IBM Journal* **1,** 239 (1957).
6. P. J. Price, *IBM Journal* **2,** 200 (1958).
7. F. S. Ham, private communication.
8. In the situation treated here, to which this statement applies, f_0 does not depend on position. For the theory of conduction in an inversion layer,[3,4] however, the operator A in (10) must be moved to the left, so as to operate on $f_0(1-f_0)$ also. For the anomalous skin effect, (10) may be generalized by including the local electric field in the space average on both sides (as well as its time dependence in (9), of course). However, in this case we are concerned specifically with the *local* current density. See, for example, V. Heine, *Phys. Rev.* **107,** 431 (1957).
9. It is not implied that this is the most physically reasonable assumption for diffuse reflection. Ham and Mattis' boundary condition corresponds to a velocity expectation $\langle v_p' \rangle = \gamma_{pz} \sqrt{(\varepsilon/2\gamma_{zz})}$ if the reflection is elastic.

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