## ON THE THEORY OF THE INFRARED ABSORPTIVITY OF METALS

## R. N. GURZHI

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

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The infrared absorptivity of metals is studied by means of the quantum kinetic equation. The quantum properties of the electromagnetic field and the anomalous character of the skin effect are taken into account.

I. In the infrared region the energy  $\hbar\omega$  of a photon is usually comparable with or greater than the imprecision kT of the Fermi level for electrons in a metal, so that a quantum method of study is required.<sup>1-3</sup> We shall first endeavor to carry through a qualitative analysis of the light absorption mechanism of a metal. In an electromagnetic field the equilibrium electron distribution function  $f_0$  (E<sub>p</sub>) is modified by an additional small term which is proportional to the field amplitude. If the electromagnetic field is regarded as classical (unquantized) the electrons cannot rise appreciably above the breadth kT of the Fermi level, because the energy acquired by an electron in a mean free path is always small compared with this quantity.

At high temperatures  $(T \gg \Theta)$  electrons are obviously able to absorb and emit phonos of all momenta up to the limit. This results in relatively high absorptivity which is proportional to the temperature.

At low temperatures  $(T \ll \Theta)$  momentum exchange is difficult. Indeed, there are almost no "large" phonons, so that they are seldom absorbed. On the other hand the majority of the electrons do not possess sufficient energy for the emission of "large" phonons, since the average electron energy above the Fermi level is of the order kT, which is small compared with k $\Theta$ . As a result there is weak absorption which decreases rapidly with temperature (~  $T^5$ ). When we take into account the quantum properties of the field an especially important difference appears in the limiting case of low temperatures and large electromagnetic quanta, when

$$\hbar\omega \gg k\Theta \gg kT. \tag{1}$$

Indeed, electrons which absorb quanta rise far above the region of the Fermi level. To be sure, they are, as previously, unable to absorb "large" phonons, but because of their high energy they can emit phonons over the entire spectrum. In this respect the quantum absorption mechanism in the limiting case (1) is similar to the classical absorption mechanism at high temperatures.

We shall here discuss the near infrared region for which

$$\omega \gg 1/\tau, \ v_0/\omega \ll \delta, \ \delta = (4\pi N e^2 / mc^2)^{-1/2}, \tag{2}$$

where  $\tau$  is the mean free time,  $\delta$  is the skin depth  $v_0/\omega$  is the distance traversed by an electron during one period of vibration of the electromagnetic field and  $v_0$  is the velocity of an electron at the Fermi level. It will also be assumed that the photoconductive threshold has not been reached. For most metals (2) is satisfied when  $\lambda \ll 100\mu$ .

Except at very high temperatures, the skin effect in the infrared region is anomalous, i.e.,

$$l = v_0 \tau > \delta. \tag{3}$$

If, however, it is assumed that the electromagnetic field and the electron distribution vary little in a mean free path  $\ell$ , for the purpose of calculating the volume absorptivity of a metal it is possible to employ perturbation theory, as was done by Holstein.<sup>2</sup> As Holstein gave a result only for the limiting case (1) and did not show his calculation, we began with a similar calculation.

In calculating the probability of photon absorption it is necessary to take into account all second-order processes with simultaneous participation of a photon and a phonon; there are 8 such processes in all. By simple calculation the expression for the volume absorptivity  $A_v$  (A = 1 - r, r is the reflection

coefficient) assumes the general form

$$A_{v} = 2\delta / c\tau (T), \tag{4}$$

after introduction of the effective mean free time

$$\tau(T) = \tau^{(cl)}(T) / \varphi(T), \tag{5}$$

where  $\tau^{(cl)}(T) \sim 1/T$  is the usual high-temperature mean free time and\*

$$\varphi(T) = \frac{2}{\alpha} \left(\frac{T}{\Theta}\right)^4 \int_0^{\Theta T} dv \cdot v^4 \left(\frac{2\alpha}{e^v - 1} + \frac{v - \alpha}{e^{v - \alpha} - 1} - \frac{v + \alpha}{e^{v + \alpha} - 1}\right), \quad \alpha = \frac{\hbar\omega}{kT}.$$
(6)

When  $kT \gg k \vartheta \gg \hbar \omega$  we necessarily have  $\varphi \approx 1$ , whereas in the other limiting case (1)  $\varphi \approx 2\Theta/5T$  and consequently,

$$\tau(T) \approx (5T/2\Theta) \tau^{\text{(cl)}}(T) = \frac{5}{2} \tau^{\text{(cl)}}(\Theta),$$

which is in agreement with Holstein's results.<sup>2</sup>

We note that (5) and (6) are obtained simply from the quantum kinetic equation derived in Ref. 1. For convenience we introduce the notation

$$\psi(E_p) = m\tau(T) D(p),$$

where  $\tau(T)$  is given by (5) and it can easily be shown that

$$\int_{0}^{\infty} dE\psi(E) = -1.$$

Then the kinetic equation (17) of Ref. 1 becomes

$$i\omega f_1 + \frac{\mathbf{p}}{m} \frac{\partial f_1}{\partial \mathbf{r}} + \hat{\tau}^{-1} f_1 = e \mathbf{E} \left[ \frac{\partial f_0}{\partial \mathbf{p}} + \frac{1}{i\omega \hat{\tau}} \frac{\partial f_0}{\partial \mathbf{p}} - \frac{\mathbf{p}}{i\omega m \tau (T)} \psi (E_p) \right].$$
(7)

The term  $(\mathbf{p}/\mathbf{m}) \partial f_1 / \partial \mathbf{r}$  drops out of a spatially uniform distribution, after which, in virtue of  $\omega \gg 1/\tau(T)$ , the kinetic equation is solved simply by successive approximations:

$$f_1^{(\mathrm{I})}(\mathbf{p}) = \frac{e}{i\omega} \left( \mathbf{E} \frac{\partial f_0}{\partial \mathbf{p}} \right), \quad f_1^{(\mathrm{II})}(\mathbf{p}) = \frac{e}{\omega^2 m \tau(T)} (\mathbf{E} \mathbf{p}) \psi(E_p), \dots$$

The first approximation naturally yields the dielectric constant

 $\varepsilon = 1 - 4\pi N e^2 / m\omega^2$ ,  $N = (8\pi / 3) (p_0 / 2\pi\hbar)^3$ 

(where N is the electron density), and the second approximation gives the conductivity

$$\sigma = Ne^2 / m\omega^2 \tau (T),$$

where, as expected,  $\tau(T)$  is given by (5). A free electron cannot absorb an electromagnetic quantum; therefore losses occur only through electron collisions with phonons (or impurities) or with the metal boundary. Since, according to (2) and (3), in the infrared region the path  $v_0/\omega$  of an electron during a period of the field vibration is small compared with the mean free path  $\ell$ , for calculation of the surface loss it is possible to neglect collisions with the lattice in first approximation. For diffuse electron reflection from the boundary the surface absorption is given by<sup>3</sup>

$$A_d = 3v_0 / 4c. \tag{8}$$

However, one must first be certain that even for very high frequencies it is possible as in Ref. 2 to simply add volume and surface losses in first approximation.

2. We now proceed to a rigorous examination of the problem with allowance for the anomalous nature of the skin effect. We first note that in the infrared region  $|\epsilon| \gg 1$ , so that it is sufficient for us to confine ourselves to normal incidence of electromagnetic waves on the surface of the metal.<sup>3</sup> Then all quantities will depend only on the distance z between any point and the metal surface.

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<sup>\*</sup>In all calculations it is assumed that kT, k $\Theta$  and  $\hbar \omega$  are small compared with the electron energy limit E<sub>0</sub>.

In momentum space we select spherical coordinates  $(p, \vartheta, \varphi)$  with the axis directed into the metal and perpendicular to its boundary, while the angle  $\varphi$  is measured from the direction of the electric field **E**.

It is known that in the case of the anomalous skin effect the electron distribution function must be subject to boundary conditions whose form depends essentially on the character of electron reflection from the metal surface. Certain theoretical considerations,<sup>3</sup> as well apparently as experiments, would indicate diffuse reflection.

diffuse reflection. We denote by  $f_1^{(1)}$  and  $f_1^{(2)}$  the respective values of  $f_1(p, z)$  for electrons reflected from  $(p_Z > 0)$  and approaching  $(p_Z < 0)$  the metal boundary. Then the condition for diffuse reflection is

$$f_1^{(1)}(\mathbf{p}, 0) = 0.$$
 (9)

In addition, we must impose the condition for vanishing of  $f_1^{(2)}$  within the metal:

$$f_{1}^{(2)}(\mathbf{p},\,\infty) = 0. \tag{10}$$

We introduce the dimensionless coordinate  $x = \omega z / v_0$  and the dimensionless quantities:

$$\eta = v_0 / \omega \delta, \quad \mathbf{x} = 1 / \omega \tau (T), \quad \hat{s} = \tau (T) / \hat{\tau}, \quad \hat{L}^{-1} = (i + \mathbf{x} \hat{s}) / \cos \vartheta$$

With this notation the kinetic equation (7) becomes

$$\hat{L}^{-1}f_1 + \partial f_1 / \partial x = (ev_0 / \omega) E(x) \chi(\mathbf{p})$$

where

)  $\chi(\mathbf{p}) = -i\hat{L}^{-1}\sin\vartheta\cos\varphi\,\partial f_0/\partial E_p + i\times\tan\vartheta\cos\varphi\cdot\psi(E_p).$ 

The general solution of this equation can be written as

$$f_{1}(\mathbf{p}, x) = e \frac{v_{0}}{\omega} \int_{0}^{x} dx' E(x') \exp\{(x' - x) \hat{L}^{-1}\} \chi(\mathbf{p})$$

Determining the lower limit of integration from the boundary conditions (9) and (10), we obtain

$$f_{1}^{(1)}(\mathbf{p}, x) = e \frac{v_{0}}{\omega} \int_{0}^{x} dx' E(x') \exp\{(x'-x) \hat{L}^{-1}\} \chi(\mathbf{p}), \quad f_{1}^{(2)}(\mathbf{p}, x) = -e \frac{v_{0}}{\omega} \int_{x}^{\infty} dx' E(x') \exp\{(x'-x) \hat{L}^{-1}\} \chi(\mathbf{p}).$$

The corresponding current density

$$j(x) = -\frac{2e}{(2\pi\hbar)^3} \left\{ \int_{p_z \ge 0} d\mathbf{p} \cdot \sin\vartheta \cos\varphi \frac{p}{m} f_1^{(1)}(\mathbf{p}, x) + \int_{p_z \le 0} d\mathbf{p} \cdot \sin\vartheta \cos\varphi \frac{p}{m} f_1^{(2)}(\mathbf{p}, x) \right\}$$

after some transformations becomes

$$j(x) = -\frac{3Ne^2}{4\pi\omega m}\int_0^{\infty} dx' E(x') \int_0^{\infty} dE_p \int_0^{2\pi} d\varphi \int_0^{\frac{N}{2}} d\vartheta \sin^2 \vartheta \cos \varphi \exp\left\{-|x-x'| \hat{L}^{-1}\right\} \chi(\mathbf{p}).$$

Inserting this expression into the equation for the electric field we obtain, since the term  $(\omega/c)^2 E$  associated with the vacuum displacement current is small in the infrared region:

$$E''(x) = \zeta \int_{0}^{\infty} dx' E(x') K(x-x'),$$
(11)

where

$$K(x) = -\frac{1}{\pi} \int_{0}^{\infty} dE_{p} \int_{0}^{2\pi} d\varphi \int_{0}^{\frac{\pi}{2}} d\vartheta \cdot \sin^{2}\vartheta \cos\varphi e^{-|x|\hat{L}^{-1}}\chi(\mathbf{p}), \quad \zeta = i \frac{3}{4} \eta^{2}.$$

An equation such as (11) is basic in the theory of the anomalous skin effect and has been thoroughly studied by Reuter and Sondheimer.<sup>4</sup>

Specifically, for the surface impedance

$$Z = R + iX = -i(4\pi v_0 / c^2) E(0) / E'(0)$$

 $Z = i \frac{4\pi v_0}{c^2} \left[ I(\zeta) \right]^{-1},$ 

Reuter and Sondheimer's results easily yield the expression

where

$$I(\zeta) = \frac{1}{\pi} \int_{0}^{\infty} dt \cdot \ln\left(1 + \zeta \frac{k(t)}{t^{2}}\right);$$
(12)

$$k(t) = \int_{-\infty}^{+\infty} dx K(x) e^{-itx} = -\frac{2}{\pi} \int_{0}^{\infty} dE_{p} \int_{0}^{2\pi} d\varphi \int_{0}^{2\pi} d\varphi \sin^{2} \vartheta \cos \varphi \frac{\hat{L}}{1 + \hat{L}^{2} t^{2}} \chi(\mathbf{p}).$$
(13)

In virtue of (2) we have for the infrared region  $|\zeta| \ll 1$ . It is therefore reasonable to attempt a representation of the surface impedance by a power series in  $\zeta$ . However, when the integrand of (12) is directly expanded in  $\zeta$  divergent expressions appear. As will be seen below, this follows particularly from the fact that the expansion does not take place in whole powers of  $\zeta$ .

For the purpose of obtaining a suitable expansion we can follow Dingle<sup>5</sup> and use the Mellin transform of  $I(\zeta)$ , which is given by

$$M(z) = \int_{0}^{\infty} d\zeta I(\zeta) \zeta^{z-1}.$$
(14)

(See Ref. 6, for example). Let the integral be bounded as follows in the region  $z_1 < \text{Re } z < z_2$ :

$$\int_{0}^{\infty} d\zeta | I(\zeta) | \zeta^{z-1} < \text{const},$$
(15)

then the inverse transformation is given by

$$I(\zeta) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} M(z) \zeta^{-z} dz$$
(16)

and exists for  $z_1 < c < z_2$ .

In our case we easily obtain from (14) and (12)

$$M(z) = \frac{1}{z \sin \pi z} \int_{0}^{\infty} dt k^{-z}(t) t^{2z}.$$

Substituting this expression into (16), we obtain after changing the sign of the integration variable

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$$I(\zeta) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} dz \, \frac{\zeta^{z}}{z \sin \pi z} \, \int_{0}^{\infty} dt k^{z}(t) \, t^{-2z},\tag{17}$$

with the condition (15) satisfied when

$$1/_{3} < \operatorname{Re} z < 1/_{2}.$$
 (18)

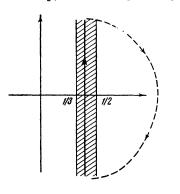
In order to obtain an expansion in increasing powers of  $\zeta$  we naturally close the integration contour at infinity in the right-hand half-plane and use the theory of residues (see the figure). However, for all z outside of the limits given by (18) the integral

$$\int_{0}^{\infty} dt k^{z}(t) t^{-2z}.$$
(19)

diverges. This difficulty can be overcome if we succeed in constructing an analytic continuation of (19), as was done in Ref. 5.

For this purpose we assume now that z lies in the zone given by (18) and write (19) in the form

$$\int_{0}^{\infty} dt k^{z}(t) t^{-2z} = \int_{0}^{1} dt k^{z}(t) t^{-2z} + \int_{1}^{\infty} dt k^{z}(t) t^{-2z}.$$
(20)



We shall also assume that we have obtained the expansion

$$k(t \le 1) = a \sum_{n=0}^{\infty} a_n t^{2^n}, \qquad k(t \ge 1) = t^{-1}b \sum_{n=0}^{\infty} b_n t^{-n}, \quad a_0 = b_0 = 1$$

and hence

$$k^{z}(t \leq 1) = a^{z} \sum_{n=0}^{\infty} A_{n}(z) t^{2n}, \qquad k^{z}(t \geq 1) = t^{-z} b^{z} \sum_{n=0}^{\infty} B_{n}(z) t^{-n}.$$
(21)

The coefficients  $A_n$  and  $B_n$  can be expressed simply in terms of  $a_n$  and  $b_n$ ; specifically,

$$A_0 = 1, \quad A_1 = a_1 z, \quad A_2 = a_2 z + \frac{1}{2} z (z+1) a_1^2, \dots$$
 (22)

Substituting the expansions (21) into the first and second integrals of (20), respectively, we obtain after integrating

$$\int_{0}^{\infty} dt \, k^{z}(t) \, t^{-2z} = \sum_{n=0}^{\infty} \left( \frac{a^{z} A_{n}(z)}{2n - 2z + 1} + \frac{b^{z} B_{n}(z)}{3z + n - 1} \right).$$
<sup>(23)</sup>

For the integration it was assumed that (18) is fulfilled, although the final result, unlike the integral on the left, is analytic over the entire z plane.

This analytic continuation can be written in a somewhat different form. We note that the lower limit 0 did not contribute to the integral in (20). Therefore the analytic continuation (23) can be written as

$$\int_{0}^{\infty} dt \, k^{z}\left(t\right) t^{-2z}.\tag{24}$$

The arbitrary constant in the original function

$$\Psi(x, z) = \int_{0}^{x} dt \, k^{z}(t) \, t^{-2z}$$

is derived from the condition that  $\Psi(0, z)$  vanish in the region (18), since otherwise (24) obviously is meaningless.

Substituting (23) into (17) we have

$$I(\zeta) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} dz - \frac{a^{z}\zeta^{z}}{z\sin\pi z} \sum_{n=0}^{\infty} \frac{A_{n}(z)}{2n-2z+1} + \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} dz \frac{b^{z}\zeta^{z}}{z\sin\pi z} \sum_{n=0}^{\infty} \frac{B_{n}(z)}{3z+n-1}.$$

When the integration contour is closed on the right-hand side (see figure) it encloses the zones for  $\sin \pi z$  at z = 1, 2, 3... and, for the first term, the zones z = (2n + 1)/2 (n = 0, 1, 2...). A complication appears in the fact that, whereas the coefficients  $A_n$  are easily obtained, the coefficients  $B_n$  cannot be given in explicit form. Indeed, according to (2)  $\kappa \ll 1$ , and thus  $\hat{L} = (i + \kappa \hat{s})^{-1} \cos \vartheta \approx -i \cos \vartheta$  is a bounded quantity. Therefore in (13) an expansion in  $\hat{L}t$  is possible for small t. On the other hand, when  $t \gg 1$   $\hat{L}t$  cannot be regarded as large, so that an expansion in  $(\hat{L}t)^{-1}$  is not permissible. In Dingle's classical treatment<sup>5</sup> a number replaced the operator  $\hat{L}$ , so that it was possible to integrate in (13) and then expand the result in reciprocal powers of t.

We shall first take the residues at the poles z = (2n + 1)/2, and in calculating the residues due to  $\sin \pi z$  we shall use Eq. (24) for the analytic continuation. The result is

$$I(\zeta) = (a\zeta)^{1/2} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} (a\zeta)^n A_n\left(n+\frac{1}{2}\right) - \frac{1}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \zeta^n \int_{-\infty}^{\infty} dt \ k^n(t) \ t^{-2n}.$$

If the integration contour were closed in the left-hand half-plane it would be possible in exactly the same way to obtain an expansion in reciprocal powers of  $\zeta$ , which would correspond to the radio frequency range. But it would be necessary to know an explicit form of the B<sub>n</sub>.

Expanding (13) in powers of  $(\hat{Lt})^2$ , we obtain

$$a = -\frac{2}{\pi} \int_{0}^{\infty} dE \int_{0}^{2\pi} d\varphi \int_{0}^{\frac{\pi}{2}} d\vartheta \sin^{2} \vartheta \cos \varphi \hat{L} \chi (\mathbf{p}), \quad a_{n} = -\frac{(-1)^{n}}{a} - \frac{2}{\pi} \int_{0}^{\infty} dE \int_{0}^{2\pi} d\varphi \int_{0}^{\frac{\pi}{2}} d\vartheta \sin^{2} \vartheta \cos \varphi \hat{L}^{2n+1} \chi (\mathbf{p}).$$

The values of  $A_n$  can be obtained from (22). Furthermore, according to (13)

$$\int_{0}^{\infty} k^{n}(t) t^{-2n} dt = (-1)^{n} \left(\frac{2}{\pi}\right)^{n} \prod_{k=1}^{n} \int_{0}^{\infty} dE_{k} \int_{0}^{2\pi} d\varphi_{k} \int_{0}^{\frac{\pi}{2}} d\varphi_{k} \sin^{2} \vartheta_{k} \cos \varphi_{k} \int_{0}^{\infty} dt \cdot t^{-2n} \frac{\hat{L}_{k}^{-1}}{t^{2} + \hat{L}_{k}^{-2}} \chi\left(\mathbf{p}_{k}\right)$$
$$= \left(\frac{2}{\pi}\right)^{n} \prod_{k=1}^{n} \int_{0}^{\infty} dE_{k} \int_{0}^{2\pi} d\varphi_{k} \int_{0}^{\frac{\pi}{2}} d\vartheta_{k} \sin^{2} \vartheta_{k} \cos \varphi_{k} \hat{L}_{k}^{-1} \sum_{m=1}^{n} \int_{0}^{\infty} dt \left[\frac{\hat{\alpha}_{mn}}{t^{2} + \hat{L}_{m}^{-2}} + \hat{\beta}_{mn} t^{-2m}\right] \chi(\mathbf{p}_{k}),$$

where

$$\hat{\alpha}_{mn} = \hat{L}_m^{2n} \prod_{i=1}^{n'} (\hat{L}_i^{-2} - \hat{L}_m^{-2})^{-1};$$

the prime denotes that the product includes no factor with i = m. From our definition of the original function

$$\int_{0}^{\infty} dt \cdot t^{-2m} = \frac{t^{1-2m}}{1-2m} \Big|_{\infty}^{\infty} = 0, \qquad \int_{0}^{\infty} \frac{dt}{t^{2} + \hat{L}^{-2}} = \frac{\pi}{2} \hat{L}$$

Thus

$$\int_{0}^{\infty} dt \cdot k^{n}(t) t^{-2n} = + \left(\frac{2}{\pi}\right)^{n-1} \prod_{k=1}^{n} \int_{0}^{\infty} dE_{k} \int_{0}^{2\pi} d\varphi_{k} \int_{0}^{\frac{\pi}{2}} d\vartheta_{k} \sin^{2} \vartheta \cos \varphi_{k} \hat{L}_{k}^{-1} \sum_{m=1}^{n} \hat{L}_{m}^{2n+1} \prod_{i=1}^{n} (\hat{L}_{i}^{-2} - \hat{L}_{m}^{-2})^{-1} \chi(\mathbf{p}_{k})$$

When  $\hat{L} = (i + \kappa \hat{s})^{-1} \cos \vartheta$  and  $\zeta = i3\eta^2/4$  are substituted in these expressions  $I(\zeta)$  can easily be represented as a series in the small dimensionless parameters  $\eta$  and  $\kappa$ . Limiting ourselves to quadratic terms in  $\eta$  and  $\kappa$ , we obtain after some tedious calculations

$$A \approx \frac{c}{\pi} R = \frac{3}{4} \beta + 2\beta \eta^{-1} \varkappa - \frac{1}{4} \beta \eta^2 \left( \frac{16}{35} \ln 2 + \frac{8723}{26880} \right) - 3\beta \eta \varkappa \left[ \frac{83}{1720} + \Phi \left( \frac{3}{8} \hat{s} \cos \vartheta - \hat{s} \cos^2 \vartheta - \cos \vartheta \hat{s} \cos \vartheta , \frac{\partial f_0}{\partial E} \right) \right] + 3\beta \varkappa^2 \left[ \Phi \left( \hat{s}^2 \cos \vartheta - \hat{s} \cos \vartheta , \frac{\partial f_0}{\partial E} \right) + \Phi \left( \hat{s} \cos \vartheta + \cos \vartheta \hat{s} - \frac{3}{8} \hat{s} , \psi \right) \right] - 3\beta \eta^{-1} \varkappa^3 \left[ \frac{5}{12} + \Phi \left( \frac{3}{2} \hat{s} - \hat{s}^2 , \psi \right) \right],$$
(25)

$$\frac{c}{\pi}X = 4\beta\eta^{-1} + \frac{83}{320}\beta\eta - 3\beta\star\Phi\left(\hat{s}\cos\vartheta, \frac{\partial f_0}{\partial E}\right) - \frac{3}{2}\beta\eta^{-1}\star^2\left[1 + 2\Phi\left(\hat{s},\psi\right)\right].$$
(26)

Here  $\beta = v_0/c$ ,  $\eta = v_0/\omega\delta$ ,  $\kappa = 1/\omega\tau(T)$  and  $\Phi$  denotes integrals of the form

$$\Phi(\hat{s}, \psi) = \frac{1}{\pi} \int_{0}^{\infty} dE \int_{0}^{2\pi} d\varphi \int_{0}^{\frac{\pi}{2}} d\vartheta \sin^{2} \vartheta \cdot \cos \varphi \cdot \hat{s} \sin \vartheta \cdot \cos \varphi \cdot \psi (E_{p})$$

It is easily seen that when the operator  $\hat{s}$  is replaced by unity (25) and (26) go over into the corresponding expressions which were obtained in a classical treatment by Dingle.<sup>7</sup> The first term in (25) coincides with (8) and thus gives the loss associated with electron reflection from the metal boundary, whereas the second term coincides with (4) and thus gives the exchange loss. Thus in first approximation we actually have a simple addition of exchange and surface losses.

All of the integrals  $\Phi$  are of the order of unity and can be calculated without great difficulty. However, the corresponding expressions cannot be written in compact form. We note that the ratio  $(\eta/\kappa)^2 = (\ell/\delta)^2$  for most good conductors is large compared with unity.\* Therefore in (25) the first two corrections, which are proportional to  $\eta^2$  and  $\eta\kappa$ , are usually most important. A calculation shows that

\*For example, for Cu, Ag and Au  $(l/\delta)^2 \sim 10$  even at room temperature.

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$$\mathbb{P}\left(\frac{3}{8}\,\hat{s}\cos\vartheta - \hat{s}\cos^2\vartheta - \cos\vartheta\,\hat{s}\cos\vartheta,\,\frac{\partial f_0}{\partial E}\right) = \frac{1}{\varphi\left(T\right)}\left(\frac{T}{\Theta}\right)^4 \int_0^{\Theta/T} dv \cdot v^4 \frac{1}{1920} \left[484 - 569v^2\left(\frac{kT}{\mu\rho_0}\right)^2\right] \\
\times \left[2\cosh\frac{v}{2} - \coth\frac{\alpha+v}{2} + \coth\frac{\alpha-v}{2} + \frac{2\left(\alpha+v\right)e^{\alpha+v}}{\left(e^{\alpha+v}-1\right)^2} - \frac{2\left(\alpha-v\right)e^{\alpha-v}}{\left(e^{\alpha-v}-1\right)^2}\right].$$
(27)

It has already been mentioned that in the infrared region we usually have  $\hbar \omega > kT$ . We therefore assume that

$$e^{\hbar\omega/hT} \gg 1, \quad e^{\hbar\omega/hT} \gg e^{\Theta/T}.$$
 (28)

Then when terms of the order of  $e^{-\hbar \omega/kT}$  are neglected the integral in (27) is greatly simplified and in our approximation  $(\eta^2 \gg \kappa^2)$  the absorption becomes

$$A \approx \frac{3}{4}\beta + 2\beta\eta^{-1}\varkappa - \frac{1}{4}\beta\eta^{2} \Big(\frac{16}{35}\ln 2 + \frac{8723}{26880}\Big) - \beta\eta\varkappa \Big\{\frac{83}{640} + \frac{1}{\varphi(T)} \Big(\frac{T}{\Theta}\Big)^{4} \int_{0}^{\Theta/T} dv \cdot v^{4} \coth \frac{v}{2} \cdot \frac{1}{320} \Big[484 - 569 \cdot v^{2} \left(\frac{kT}{\mu\rho_{0}}\right)^{2}\Big]\Big\}.$$

On the basis of (27) in the classical limit ( $\hbar \omega \ll k\Theta \ll kT$ ) we easily obtain the following expression for the second absorption correction:

$$- \beta \eta \varkappa \frac{1}{640} \left[ 567 - \frac{2}{3} 569 \left( \frac{k\Theta}{u p_0} \right)^2 \right].$$

If we immediately set  $\hat{s} = 1$  in (25) the result is  $-\beta\eta\kappa 83/12$ , which agrees with the corresponding term in Ref. 7. It appears that in Ref. 7 all corrections beginning with the second were calculated incorrectly, because even when  $\hbar \omega \ll kT$  it is not always correct in the case of the anomalous skin effect to approximate the collision integral by means of an expression of the form  $f_1/\tau$  (see the comment at the end of Ref. 8).

When the inequalities (28) are fulfilled it follows from (6) that

$$\varphi(T) \approx 2\left(\frac{T}{\Theta}\right)^4 \int_{0}^{\Theta/T} dv \, v^4 \coth \frac{v}{2} - \frac{\Theta}{3T} \frac{k\Theta}{\hbar\omega}.$$
(29)

An investigation of this expression shows that from room temperature down to the temperature of liquid helium the mean free time  $\tau(T) = \tau^{(Cl)}(T)/\varphi(T)$  is relatively independent of temperature and changes smoothly from  $\tau^{(Cl)}(T)$  at high temperatures to  $\frac{5}{2} \tau^{(Cl)}(\Theta)$  at low temperatures. Classically, as we know,  $\tau(T)$  increases very rapidly as the temperature is reduced (at low temperatures it is inversely proportional to  $T^5$ ). It is significant that (29) was derived subject to the relatively mild limitations of (28); therefore quantum effects play an important part at least when  $\hbar \omega \sim (2-3) kT$ .

It must be remembered that the results obtained here are based on the assumption of a spherical Fermi surface for the electrons of a metal and can apparently be applied only to polycrystalline specimens. Of course, m and  $v_0$  mean averaged quantities. In addition, and especially at low temperatures, interelectronic collisions may play a large role. This question will be discussed at a later date.

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