

OPTICAL PROPERTIES OF METALS IN THE CASE OF A WEAKLY ANOMALOUS SKIN EFFECT

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A relation is established between the reciprocal of the effective dielectric constant and microcharacteristics of a metal in the case of weak anomalous skin effect. The isotropic case (polycrystalline substances) and cubic single crystals with a four-fold symmetry axis perpendicular to the surface of the metal are considered. Such cases are encountered in metals with a low Debye temperature (In, Pb, Sn, etc.) and also in metals or alloys with a high residual resistance. The experimental data are analyzed for In and Pb.

AN experimental investigation of the optical constants of many metals in the infrared region has shown that in many cases there is a weakly pronounced anomalous skin effect at room temperature<sup>[1-3]</sup>. The point is that for many metals in which the interaction between the electrons and phonons is large (these metals usually have a Debye temperature  $\Theta$  below room temperature), the mean free path of the electron  $l$  is to be sure smaller than the skin-layer depth  $\delta$ , but both quantities are of the same order of magnitude. It is necessary here to take into account the reflection of the electrons from the surface of the metal<sup>1)</sup>, but such account can be carried out accurate to terms of first order relative to the quantity  $(v/c)\sqrt{\epsilon}/(1 - i\nu/\omega)$ . Here  $v$ —velocity of the electrons on the Fermi surface,  $c$ —velocity of light,  $\epsilon = (n - i\kappa)^2$ —complex dielectric constant,  $\nu$ —effective electron collision frequency, and  $\omega$ —cyclic frequency of light.

1. Let us consider normal incidence of light on a metal. The surface of the metal is perpendicular to the  $z$  axis. The metal occupies the half-space  $z > 0$ . The equilibrium distribution function  $f_0$  of the electrons in the metal is a Fermi function. We denote by  $f$  the increment of

the equilibrium function. We confine ourselves to the case when the direction of the field in the metal  $\mathbf{E}$  coincides with the direction of the current density  $\mathbf{j}$  (isotropic case or case of cubic symmetry with four-fold symmetry axis perpendicular to the metal surface)<sup>2)</sup>. Let  $\mathbf{E} \equiv E_x$ , so that  $\mathbf{j} \equiv j_x$ .

The initial system of equations for  $f$  and  $E$  is<sup>[5]</sup>

$$v_z \partial f / \partial z + (i\omega + \nu)f = -eE \partial f_0 / \partial p_x, \tag{1}$$

$$d^2 E / dz^2 + \omega^2 E / c^2 = i4\pi\omega j / c, \tag{2}$$

$$j = \frac{2e}{(2\pi\hbar)^3} \int v_x f d\mathbf{p}, \quad d\mathbf{p} = dp_x dp_y dp_z. \tag{3}$$

Here  $e$ —electron charge,  $\mathbf{p}$ —electron momentum,  $v$ —electron velocity. The time dependence is given by  $e^{i\omega t}$ . The electron collision frequency  $\nu$  can generally speaking depend on  $\omega$ . No limitations are imposed on the ratio  $\nu/\omega$ . In the cases of interest to us this ratio is close to unity.

The system (1)–(3) is solved by successive approximations. In the zeroth approximation we neglect in (1) the term  $v_z \partial f / \partial z$ , after which we obtain the well-known case of normal skin effect<sup>[5]</sup>. The solution of the system (1)–(3) in the zeroth approximation yields

$$E = E(0) \exp[-i\omega \sqrt{\epsilon_0} z / c]. \tag{4}$$

$$\epsilon_0 - 1 = -\frac{8\pi e^2}{(2\pi\hbar)^3 \omega (\omega - i\nu)} \oint \frac{v_x^2}{v} ds = -\frac{4\pi e^2}{\omega(\omega - i\nu)} \frac{N}{m}. \tag{5}$$

Here  $E(0)$  is the field on the surface of the metal,

<sup>1)</sup>In our earlier papers<sup>[1,2]</sup> we used relations connecting  $\text{Re } \epsilon^{-1}$  and  $\text{Im } \epsilon^{-1}$  with  $N$  and  $\nu$  for the normal skin effect. The correction for the anomaly of the skin effect was introduced only in the expression for  $\text{Im } \epsilon^{-1}$  by adding to  $\nu$  the frequency of the collisions between the electrons and the surface, for which an expression obtained in the case of a sharply pronounced anomalous skin effect was used. This account of the anomaly of the skin effect is only tentative. In the present paper we determine it more consistently with the degree of accuracy indicated above.

<sup>2)</sup>The case of arbitrary anisotropy was considered in<sup>[4]</sup>. The authors were interested, however, only in the region  $\nu \ll \omega$ .

$\epsilon_0 = (n_0 - i\kappa_0)^2$ —the complex dielectric constant in the case of normal skin effect,  $N$ —concentration of the conduction electrons,  $m$ —mass of free electrons,  $ds$ —element of Fermi surface. For a cubic crystal

$$\oint \frac{v_x^2}{v} ds = \oint \frac{v_y^2}{v} ds = \oint \frac{v_z^2}{v} ds = \frac{1}{3} \oint v ds,$$

therefore

$$\frac{N}{m} = \frac{2}{(2\pi\hbar)^3} \oint \frac{v_x^2}{v} ds = \frac{2}{3(2\pi\hbar)^3} \oint v ds = \frac{2\langle v \rangle S}{3(2\pi\hbar)^3} \quad (5')$$

where  $\langle v \rangle$ —mean value of the velocity on the Fermi surface and  $S$ —area of the Fermi surface. The ratio (5') serves as a definition of  $N$ .<sup>3)</sup> For a spherical Fermi surface

$$N/m = 8\pi m_{\text{eff}}^2 v^3 / 3(2\pi\hbar)^3, \quad (6)$$

where  $m_{\text{eff}}$ —effective mass of the electron.

Substituting (4) in (1) we obtain the first-approximation equation. For the boundary conditions we use conditions corresponding to diffuse reflection of the electrons from the surface of the metal

$$\begin{aligned} f &= 0 \text{ for } v_z > 0 \text{ when } z = 0; \\ f &= 0 \text{ for } v_z < 0 \text{ when } z \rightarrow \infty. \end{aligned} \quad (7)$$

The calculations then proceed as follows. We determine  $f$  from (1) and (7). We obtain  $j$  by using (3). We then calculate the total current

$I = \int_{-\infty}^{\infty} j(z) dz$  and the surface impedance

$Z = E(0)/I$ . The latter is connected with the effective complex dielectric constant  $\epsilon = (n - i\kappa)^2$  by the relation  $Z = 4\pi/c\sqrt{\epsilon}$ . As a result we get<sup>4)</sup>

<sup>3)</sup>Sometimes one introduces in place of  $N$  a quantity  $N'$  defined by  $N'/m_{\text{eff}} = N/m$ . For simplicity we shall use  $N$ .

<sup>4)</sup>For metals of cubic symmetry with arbitrary crystal orientation relative to the metal surface, the current  $I$  coincides in first approximation with the direction of the field  $E$  on the surface of the metal. In first approximation, in the presence of a field  $E_x$ , both  $I_x$  and  $I_y$  will differ from zero. It is easy to ascertain that, with the accuracy indicated,

$$\frac{I_y}{I_x^0} = \frac{i\omega}{c} \frac{n - i\kappa}{i\omega + \nu} \oint_{v_z > 0} \frac{v_x v_y v_z}{v} ds \left/ \oint \frac{v_x^2}{v} ds \right.$$

Here  $I_y$  is the total current along the  $y$  axis and  $I_x^0$  is the total current in the zeroth approximation along the  $x$  axis. It is obvious that for any orientation  $|I_y/I_x^0| < |y/2|$ . The presence of the current  $I_y$  leads to the appearance of off-diagonal terms in the surface impedance  $Z_{xy}$  and in the effective dielectric constant  $\epsilon_{xy}$ . These terms, however, are small and can be neglected in practice. In the isotropy case or in the case when the four-fold symmetry axis is perpendicular to the surface of the metal, we have  $I_y = Z_{xy} = \epsilon_{xy} = 0$ .

$$\epsilon^{-1}(1 - \gamma) = \epsilon_0^{-1}, \quad (8)$$

$$\gamma = \frac{2}{c} \frac{n - i\kappa}{1 - i\nu/\omega} \oint_{v_z > 0} \frac{v_x^2 v_z}{v} ds \left/ \oint \frac{v_x^2}{v} ds \right. \quad (9)$$

Here  $\oint_{v_z > 0}'$  denotes the integral over the part of the Fermi surface for which  $v_z > 0$ .

For a spherical Fermi surface we have

$$\gamma = \frac{3}{8} \frac{\nu}{c} \kappa \frac{\sqrt{1 + (n/\kappa)^2}}{\sqrt{1 + (\nu/\omega)^2}} e^{i(\varphi_1 - \varphi_2)}, \quad (10)$$

where  $\tan \varphi_1 = n/\kappa$  and  $\tan \varphi_2 = \omega/\nu$ .

Using (8), (10), and (5), and neglecting terms of order  $1/|\epsilon_0|$ , we get

$$\lambda_\mu^2 \frac{\kappa^2 - n^2}{(n^2 + \kappa^2)^2} (1 - \beta_1) = \frac{0.1115}{N} 10^{22}, \quad (11)$$

$$\lambda_\mu \frac{2n\kappa}{(n^2 + \kappa^2)^2} (1 - \beta_2) = 5.918 \cdot 10^5 \frac{\nu}{N}, \quad (12)$$

$$\beta_1 = \text{Re } \gamma + \frac{2n\kappa}{\kappa^2 - n^2} \text{Im } \gamma, \quad (13)$$

$$\beta_2 = \text{Re } \gamma - \frac{\kappa^2 - n^2}{2n\kappa} \text{Im } \gamma. \quad (14)$$

Here  $\lambda_\mu$ —wavelength of light in microns.

Formulas (10)–(14) can serve for the determination of the microcharacteristics of the metal  $N$ ,  $\nu$ , and  $v^5$ . A convenient procedure is as follows. First we determine  $N$  and  $\nu$  in the zeroth approximation, putting  $\beta_1 = \beta_2 = 0$ . Then these values of  $N$  and  $\nu$  are used to calculate  $\beta_1$  and  $\beta_2$ , choosing  $\nu$  such that the left half of (11) is independent of  $\lambda_\mu$ . It is then possible to determine  $N$  and  $\nu$  in the first approximation.

Usually  $\varphi_1 - \varphi_2 < 0$  and  $\beta_1 < \beta_2$ , so that the correction is much more important in the determination of  $\nu$  than in the determination of  $N$ .

2. We shall employ the foregoing methods to

<sup>5)</sup>The isotropic case is in practice the most significant not only because most measurements of optical constants in the infrared region are made with polycrystalline specimens, but also because the distribution of the electrons in the metals can be regarded in first approximation as isotropic. Investigations of cyclotron resonance, the deHaas–van Alphen effect, etc. confirm the distribution of the Fermi surface over the bands, obtained by starting with the free-electron representation. All that is refined are the individual sections located near the boundaries of the Brillouin zones. These parts pertain to small groups of the electrons, which influence little the optical constants of the metals in the infrared region. We assume that in order to describe the optical properties of metals in the region  $\lambda > 1 \mu$  it is possible to assume with good accuracy, that the distribution of the electrons is isotropic (it is assumed that the internal photoeffect does not lie in the indicated interval).

Table I. Optical constants and microscopic characteristics of indium at  $T = 293^\circ\text{K}$

$\lambda_\mu$	$n$	$\kappa$	$\lambda_\mu^2 \frac{\kappa^2 - n^2}{(n^2 + \kappa^2)^2} \cdot 10^2$	$\lambda_\mu \frac{2n\kappa}{(n^2 + \kappa^2)^2} \cdot 10^3$	$\beta_1 \cdot 10^2$	$\beta_2 \cdot 10^2$	$N \cdot 10^{-22}$	$\nu \cdot 10^{-11}$
2.5	3.19	13.7	2.83	5.58	0.4	3.5	3.96	3.60
3.0	4.26	16.4	2.74	5.09	0.5	3.7	4.11	3.39
4.0	6.57	20.8	2.75	4.83	0.8	3.7	4.10	3.21
5.0	9.03	24.8	2.75	4.62	1.1	3.7	4.12	3.08
6.0	11.7	28.1	2.74	4.51	1.4	3.5	4.15	3.10
7.0	14.1	30.9	2.78	4.58	1.8	3.4	4.09	3.06
8.0	16.4	33.6	2.82	4.51	2.1	3.2	4.06	2.99
9.0	18.7	35.8	2.84	4.53	2.3	3.1	4.04	2.99
10.0	21.0	37.4	2.83	4.64	2.6	2.8	4.06	3.09
11.0	23.2	39.2	2.81	4.65	2.9	2.7	4.11	3.13
12.0	24.6	40.5	2.96	4.74	3.1	2.5	3.90	3.04

reduce the experimental data on the optical constants of In and Pb, published in our earlier papers.<sup>[1,2]</sup> The measurements were carried out with polycrystalline specimens. The optical constants of the indium were measured in [1]. The results are listed in Table I.

In order for the left half of (11) to be independent of  $\lambda_\mu$ , we must put  $v \approx 3 \times 10^8$  cm/sec. Since the scatter of the experimental data for different values of  $\lambda_\mu$  is rather large,  $v$  was determined accurate to  $\approx 30\%$ . In the zeroth approximation for  $N$  we have taken the average value obtained from the formulas of the normal skin effect,  $N_0 = 6.2 \times 10^{22}$  cm<sup>-3</sup>. The value of  $\nu$  in the zeroth approximation was calculated for each wavelength.

In determining the microcharacteristics of indium we have used the spectral interval 2.68–10.0  $\mu$ . The optical constants of the shorter-wavelength points are influenced by the additional absorption band with a maximum located approximately in the region of 0.7  $\mu$ . A more accurate determination of the position of the maximum of this band calls for measurements in the visible region, which were not carried out. Indium has three valence electrons per atom: two s-electrons and one p-electron. The p-electrons emerge to the Fermi surface, while the s electrons fill the first band completely. It is probable that the absorption maximum indicated above is connected with the transition of the s-electrons to the Fermi surface (internal photoeffect).

It follows from Table I that the average conduction-electron concentration is  $\langle N \rangle = 6.3 \times 10^{22}$  cm<sup>-3</sup>, which almost coincides with the value obtained by the formulas of the normal skin effect. The surface losses amount to approximately 15% of the total losses. The effective frequency of the electron collisions  $\nu$  depends on  $\omega$ . This dependence can be substituted in the form  $\nu = \nu_0 + a/\lambda^2$ , with  $\nu_0 = 2.2 \times 10^{14}$  sec<sup>-1</sup> and  $a = 7.0 \times 10^{14}$   $\mu^2$

sec<sup>-1</sup>. If we assume that the quadratic term is determined by the frequency of the collisions between electrons (see [1]), then we obtain for the static value of this frequency  $\nu_0^{\text{ee}} = 1.1 \times 10^{13}$  sec<sup>-1</sup>.

The static conductivity of the investigated indium mirrors was  $\sigma = 0.64 \times 10^{17}$  cgs esu. The static electron collision frequency determined from this is  $\nu^{\text{st}} = 2.5 \times 10^{14}$  sec<sup>-1</sup>. This is somewhat larger than the value of  $\nu_0$ , probably because of the inaccuracy in the determination of  $\sigma$  (both  $\nu_0$  and  $\nu^{\text{st}}$  include the frequency of collisions with the impurities, which can be determined from the value of the residual resistance; see [1]). The microcharacteristics connected with the electron collision frequencies and also the values of  $v$  obtained by the method proposed above differ somewhat from those obtained in [1], owing to the more accurate account of the influence of the anomaly of the skin effect in this work. For indium at room temperature  $\nu \approx \omega$  at a wavelength of light  $\lambda_\mu \approx 8\mu$ .

We process analogously the values of the optical constants of lead, obtained experimentally in [2]. The results are listed in Table II.

The requirement that the left half of (11) be independent of  $\lambda_\mu$  is satisfied when  $v = 1.0 \times 10^8$  cm/sec. The scatter in the experimental values for the left half of (11) for different  $\lambda_\mu$  is small, making it possible to determine  $v$  accurate to  $\approx 10\%$ . In the zeroth approximation we have chosen for  $N$  the average value obtained from the normal skin effect formulas,  $N_0 = 4.0 \times 10^{22}$  cm<sup>-3</sup>. The value of  $\nu$  was calculated in the zeroth approximation for each wavelength of light.

To determine the microscopic characteristics of lead, the spectral interval 2.5–12  $\mu$  was used. As in the case of indium, the optical constants of the shorter wavelength points were influenced by an additional absorption band the maximum of

Table II. Optical constants and microscopic characteristics of lead at  $T = 293^\circ\text{K}$

$\lambda_\mu$	$n$	$\kappa$	$\lambda_\mu^2 \frac{\kappa^2 - n^2}{(n^2 + \kappa^2)^2} \cdot 10^3$	$\lambda_\mu \frac{2n\kappa}{(n^2 + \kappa^2)^2} \cdot 10^3$	$\beta_1 \cdot 10^2$	$\beta_2 \cdot 10^2$	$N \cdot 10^{-22}$	$\nu \cdot 10^{-14}$
2.68	4.43	18.2	1.82	3.51	1.7	13.1	6.24	3.21
3.14	5.50	21.2	1.80	3.18	2.0	14.3	6.34	2.91
4.00	7.60	26.1	1.83	2.91	2.9	15.3	6.28	2.62
5.95	13.4	35.6	1.84	2.71	5.1	15.0	6.38	2.48
8.0	19.2	42.2	1.96	2.81	7.5	12.9	6.18	2.55
10.0	23.8	51.7	2.01	2.34	9.3	15.1	6.15	2.05

which lies in the region near  $0.7 \mu$ . The position of this maximum was not determined accurately, since it calls for additional measurements in the visible region. Lead has four valence electrons: two s electrons and two p electrons. Two electrons fill completely the first band (these are probably s electrons). The remaining two electrons are situated principally in the second and third bands [6]. It can be assumed that the additional band corresponds to the internal photoeffect, which transfers the electrons from the first band to the Fermi surface. The main part of the Fermi surface of lead is located in the second and third bands. The second band corresponds to holes and the third to electrons. The assignment of part of the Fermi surface to electrons and part to holes does not influence the value of  $\epsilon$ , since  $\epsilon \sim e^2$ .

However, if we assume such a breakdown of the Fermi surface into two parts, then we must assume that the optical measurements yield

$$N/m = N^e/m_{\text{eff}}^e + N^h/m_{\text{eff}}^h,$$

where  $N^e/m_{\text{eff}}^e$  and  $N^h/m_{\text{eff}}^h$  are determined by integrals of the type  $\int v_x^2 ds/v$  over the parts of the Fermi surface pertaining to the electrons and holes, respectively.

It follows from Table II that the average value of  $N$  is  $\langle N \rangle = 4.1 \times 10^{22} \text{ cm}^{-3}$ , which almost coincides with the value obtained by the formulas of the normal skin effect. The surface losses amount to merely 3–4% of the total losses. In the long-wave region, the effective electron collision frequency  $\nu$  is practically independent of the frequency of light. It is impossible to separate the quadratic term connected with the collisions between electrons. A noticeable influence is exerted on the short-wave region by the internal photoeffect [6]. The static conductivity of the in-

vestigated mirrors is  $\sigma = 0.41 \times 10^{17} \text{ cgs esu}$ , which gives a static collision frequency  $\nu^{\text{st}} = 2.5 \times 10^{14} \text{ sec}^{-1}$ . Optical measurements give an average value of the collision frequency for the long-wave region  $\langle \nu \rangle = 3.1 \times 10^{14} \text{ sec}^{-1}$ , that is, a noticeably larger quantity. The difference cannot be attributed to the error in the measurement of  $\sigma$ , which in the case of lead has been measured with great accuracy. It can likewise not be attributed to quantum effects, since the Debye temperature for lead is  $\Theta = 86^\circ\text{K}$ , which is much lower than room temperature, and in this case the quantum value for the collision frequency coincides with its classical value [8]. We assume that the reason lies in the different influence exerted by the short-wave part of the acoustical spectrum on the optical constants and on the static conductivity.

It is easy to verify that  $l < \delta_n$  for both metals.

Thus, for metals characterized by strong interaction between the electrons and phonons (these metals usually have a low Debye temperature), the character of the skin effect at room temperature is weakly anomalous and we can take account of this anomaly by the method proposed above.

The method indicated in the present work is applicable not only to metals with low Debye temperature, but also to metals or alloys in which the residual resistivity is large. In this case the mean free path, determined by the collision with the impurities or with the lattice defects can also be smaller than the depth of the skin layer.

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<sup>6</sup>In our preceding investigation [2,3] we have not paid sufficient attention to the internal photoeffect, and this led to an erroneous determination of the frequency of the collisions between electrons.

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