

# The Behavior of Metals at Optical Frequencies

Jeff Clark

November 30, 2004

## **I. Introduction**

Metals, like any other solid, are composed of atoms that may or may not form a periodic lattice. Regardless of the specific arrangement, this theory predicts that as the frequency of an incident electromagnetic wave approaches infinity, meaning that the wavelength approaches zero, the wave propagates through any material (metals included) as if there were in fact no material present. That is, for incident radiation of zero wavelength all materials act like a vacuum. However, it is obvious that for finite frequencies materials do not generally act like a vacuum. For sufficiently low frequencies, metals act as nearly perfect conductors reflecting almost all incident radiation. Of interest, then, is that range of frequencies where the metal makes the transition from being a nearly perfect conductor to a transparent material. The span of frequencies broadly labeled 'optical' are worthy of note in this regard.

This paper presents a brief review of the theory related to the behavior of metals at optical frequencies: infrared (IR), visible, ultra-violet (UV). The discussion shall start with a very simple model and then progressively refine the approach to take account of some of the empirically observed characteristics.

## **II. The Ideal Conductor**

The simplest model of metals is based on the assumption that they are perfect electric conductors over all frequencies. In this case, the reflectivity (or the reflection coefficient,  $R$ ) is always unity regardless of frequency. Of course, as mentioned in the introduction, this is not a realistic model. Nevertheless, for applications where the wavelength is relatively long and where high accuracy is not required, this model suffices. A more refined model considers the nature of the constituent elements of the material.

### III. The Drude Model

The Drude free-electron model provides a much more realistic and interesting model of metal behavior than does the ideal conductor model. The Drude model is classical in its approach and considers the material to be a ‘gas’ of free electrons interspersed among some arrangement of relatively heavy positive ions. Metal atoms in the solid donate their loosely bound valence electrons, and the heavy nuclei become these positive ions. The combination of these positive ionic cores and the ‘gas’ of electrons is neutral overall and is called a plasma. It is assumed that the electrons do not interact with each other or with the positive nuclei, with the exception of random electron collisions with the nuclei. These free and independent electrons may be treated as classical particles according to the following equation. (It is noteworthy that these derivations largely follow [1].)

$$m_e \frac{d^2 x}{dt^2} + m_e \gamma \frac{dx}{dt} = -e E(t) \quad (1)$$

This equation, which is an expression of  $F = ma$ , involves the mass of the electron,  $m_e$ , the electronic charge,  $e$ , and the incident electric field,  $E(t)$ . The damping factor  $\gamma$  accounts for the collisions between electrons and positive ions in the metal. It is expected that the variation of position  $x$  with time will be of the same form as the time variation of the incident field,  $E(t)$ . If this field is monochromatic, then (1) can be written as:

$$m_e \frac{d^2 x}{dt^2} + m_e \gamma \frac{dx}{dt} = -e E_0 e^{j\omega t} \quad (2)$$

with:

$$x(t) = x_0 e^{j\omega t} . \quad (3)$$

Using (3), (2) is easily solved by substitution.

$$-m_e \omega^2 x_0 e^{-j\omega t} + j m_e \gamma \omega x_0 e^{-j\omega t} = -e E_0 e^{-j\omega t} \quad (4)$$

$$x(t) = \frac{e E(t)}{m_e(\omega^2 - j \omega \gamma)} \quad (5)$$

Ignoring the possibility of excess charge on the material, a metal is a macroscopically neutral material. As a result, the displacement of an electron,  $x(t)$ , may be viewed as a dipole of charge  $e$  and length  $x(t)$ . The summation of all the dipoles formed per unit volume as a result of the incident fields is simply the electric polarization,  $P$ . If the number of electrons per unit volume is  $N$  (being the number of atoms per unit volume multiplied by the number of valence electrons in the atom), then:

$$P(t) = -Nex(t) \quad (6)$$

This result leads to the definition of the relative dielectric constant,  $\epsilon_r$ , for the metal. Obviously since (5) is complex,  $\epsilon_r$  will be complex as well. The total electric flux density,  $D$ , is given as follows, thus allowing the determination of  $\epsilon_r$ .

$$D(t) = \epsilon_0 E(t) + P(t) = \epsilon_0 E(t) - \frac{Ne^2}{m_e(\omega^2 - j\omega\gamma)} E(t) = \epsilon_0 E(t) \epsilon_r \quad (7)$$

$$\epsilon_r(\omega) = 1 - \frac{Ne^2}{m_e \epsilon_0 (\omega^2 - j\omega\gamma)} = 1 - \frac{\omega_p^2}{\omega^2 - j\omega\gamma} \quad (8)$$

In (8), the so-called plasma frequency,  $\omega_p$ , has been defined.

$$\omega_p = \left( \frac{Ne^2}{m_e \epsilon_0} \right)^{1/2} \quad (9)$$

Alternatively, an approach based on velocity instead of position may be taken. This will provide greater elucidation of these results. Equation (5) may be converted by a time derivative to a velocity.

$$v(t) = -\frac{j\omega eE(t)}{m_e(\omega^2 + j\omega\gamma)} = \frac{eE(t)}{m_e(\gamma + j\omega)} \quad (10)$$

The current density,  $J$ , is given as:

$$J = -Ne\mathbf{v} = \sigma E. \quad (11)$$

Substituting (10) into (11) yields the following.

$$J = -\frac{Ne^2}{m_e(j\omega + \gamma)} E = \sigma(\omega) E(t) \quad (12)$$

$$\sigma(\omega) = \frac{Ne^2}{m_e(j\omega + \gamma)} \quad (13)$$

The meaning of the parameter  $\gamma$  can be seen by examining the behavior of the electron momentum when the incident field is turned off. Equation (1) may be recast in terms of the momentum,  $p$ , as follows:

$$\frac{\partial p}{\partial t} = -\gamma p - eE \quad (14)$$

If the field term goes to zero, then a simple differential equation is left that has an exponential solution with initial momentum  $p_0$  as expressed below.

$$\frac{\partial p}{\partial t} = -\gamma p \quad (15)$$

$$p(t) = p_0 e^{-\gamma t} = p_0 e^{-\frac{t}{\tau}} \quad (16)$$

But (16) written in terms of  $\tau$  instead of  $\gamma$ , where  $\tau$  is  $1/\gamma$ , reveals that this is simply the decay of the momentum with  $\tau$  being a “relaxation time.” Since the only possible mechanism that could cause electron momentum to decay in this model is scattering off positive ions,  $\tau$  is called the “momentum scattering time.” [1] This is related to the collision rate for electrons in the Drude medium.

Given the interpretation for  $\tau$ , (13) may be rewritten as follows, and the DC conductivity,  $\sigma_0$ , may be written as well.

$$\sigma(\omega) = \frac{Ne^2 \tau}{m_e(1 + j\omega\tau)} \quad (17)$$

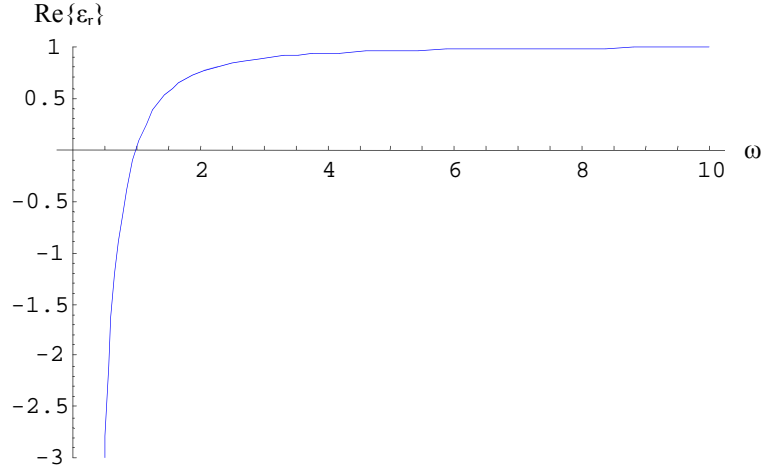
$$\sigma_0 = \frac{Ne^2 \tau}{m_e} \quad (18)$$

Combining (8) and (17) allows the relative permittivity to be written in terms of the conductivity:

$$\varepsilon_r(\omega) = 1 - \frac{j \frac{Ne^2}{m_e \varepsilon_0} \tau}{\omega j \omega \tau + 1} = 1 - j \frac{\sigma(\omega)}{\omega \varepsilon_0} \quad (19)$$

### III A. Perfect DC Conductor

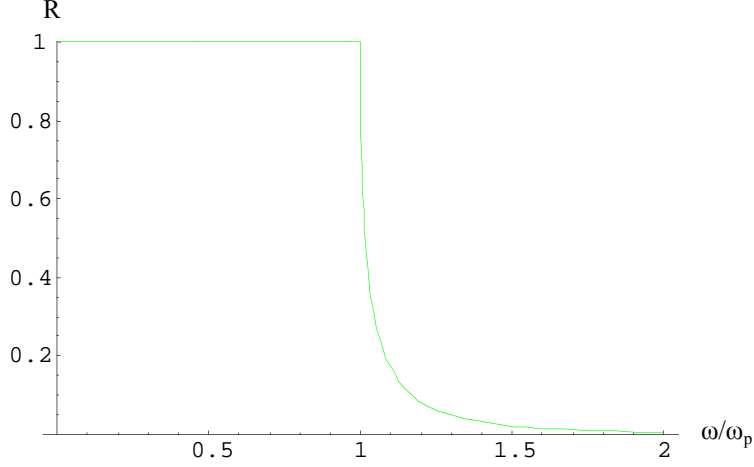
The simplest case for the above results involves when  $\tau$  goes to infinity. This is the case of a perfect conductor at DC resulting from no collisions between electrons and positive ions. For this case, it is clear from (19) that  $\varepsilon_r$  becomes entirely real as shown in Figure 1.



**Figure 1.** Plot of  $\varepsilon_r$  versus angular frequency normalized to  $\omega_p$ .  $\tau$  is  $\infty$ .

Also of interest is the reflection coefficient for normally incident plane waves (reflectivity),  $R$ , with respect to a vacuum. This value is shown below and plotted in Figure 2 over a range of angular frequencies, where  $R$  is given as the following:

$$R(\omega) = \left| \frac{\sqrt{\varepsilon_r(\omega)} - 1}{\sqrt{\varepsilon_r(\omega)} + 1} \right|^2. \quad (20)$$



**Figure 2.** The reflection coefficient  $R$  versus angular frequency normalized to  $\omega_p$ .

Interestingly, the relative permittivity of the metal is negative for frequencies below the plasma frequency. This corresponds to perfect reflection of incident waves since the index of refraction,  $n$ , is purely imaginary (assuming a non-magnetic material).

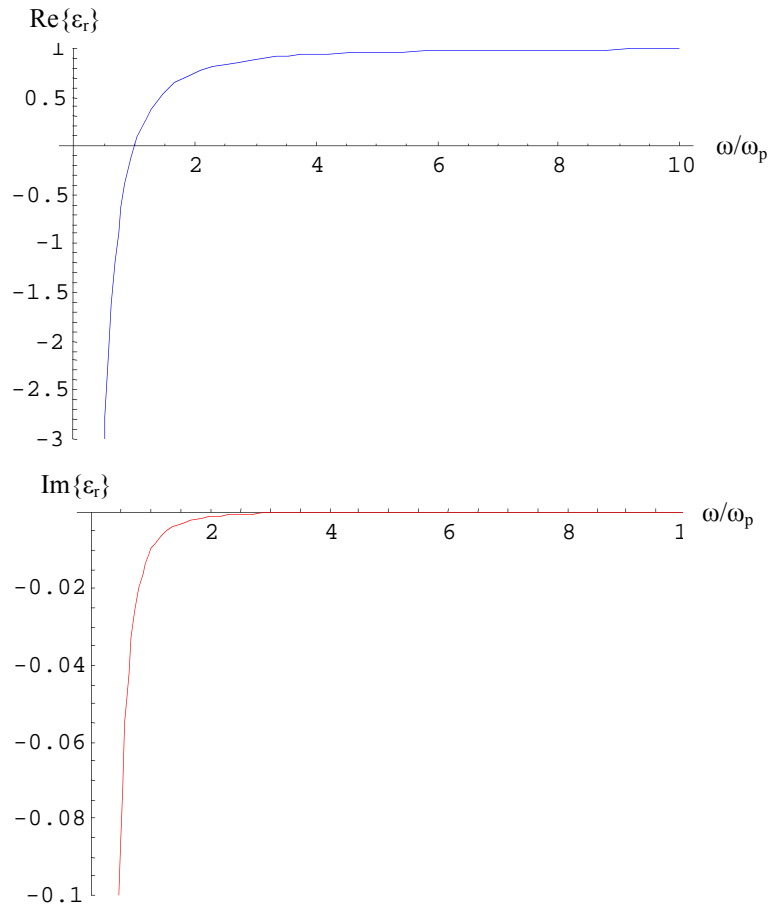
$$n(\omega) = \sqrt{\varepsilon_r(\omega)} \quad (21)$$

Above the plasma frequency, the relative permittivity becomes positive once again, causing the index of refraction to become real, and the reflection coefficient drops as the metal approaches the behavior of a vacuum. This is the expected result for very large frequencies, as was pointed out at the outset of this paper.

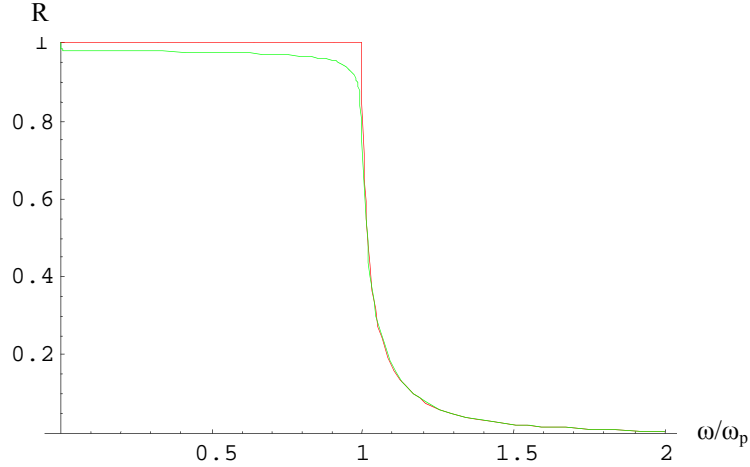
The only parameter in this case that depends upon the material is  $N$ , the number of atoms per unit volume. This determines the plasma frequency, as shown in (9). For many metals,  $N$  is on the order of  $10^{28}$  to  $10^{29}$  atoms per cubic meter, corresponding to plasma wavelengths on the order of 100nm. These values are typically well below the wavelengths of visible light, and it is therefore expected, according to this model, that metals should be perfect reflectors in the visible spectrum. Metals like silver generally bear this out. Nevertheless, that such metals as gold and copper have characteristic colors (in spite of their plasma wavelengths being shorter than those of the visible spectrum) implies that this model is not sufficient to account for the behavior of metals at visible frequencies.

### III B. Finite Conductivity at DC

The next obvious step to refine this model is to make  $\tau$ , and thus the DC conductivity  $\sigma_0$ , finite. This more realistic view accounts for the fact that electrons are not entirely free in the metal but are liable to scatter off the positive ions that also compose the material. The parameter  $\tau$  is typically on the order of  $10^{-14}$  seconds for metals. The results for  $\epsilon_r$  are shown in Figure 3, and the results for  $R$  are shown in Figure 4 for this Drude model.



**Figure 3.** Real (top) and imaginary (bottom) parts of  $\epsilon_r$  for the Drude model with  $\tau$  equal to  $10^{-14}$ . The frequency is normalized to  $\omega_p$ .



**Figure 4.** The reflection coefficient compared for  $\tau = \infty$  (upper) and  $\tau = 10^{-14}$  (lower).

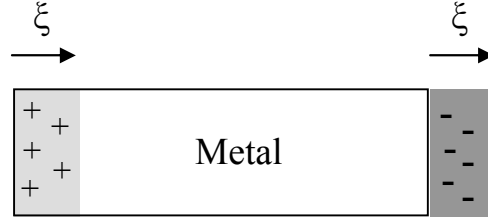
There is little variation in the relative permittivity as a result of this change in  $\tau$  (the curves very nearly overlap, so a comparison was not shown in Figure 3). However, some variation is seen in  $R$ , and the finite conductivity reveals itself as less than total reflection at frequencies below  $\omega_p$ . This results from the index of refraction,  $n$ , no longer being purely real or purely imaginary depending on the frequency; rather, it becomes complex. Below, the complex refractive index is labeled  $\hat{n}$ .

$$\hat{n}(\omega) = \sqrt{\varepsilon_r(\omega)} = n(\omega) + j\kappa(\omega) \quad (22)$$

The complex portion of the refractive index,  $\kappa$ , is often referred to as the “extinction coefficient” [2].

### III C. Plasmons

Although the behavior of the metal above and below the plasma frequency seems clear enough in this model, the behavior at the plasma frequency reveals an interesting phenomenon. If the electron ‘gas’ in the metal is displaced slightly with respect to the arrangement of positive ions, so-called plasma oscillations, or ‘plasmons,’ can occur. The displacement is depicted in Figure 5.



**Figure 5.** The displacement of the electron ‘gas’ relative to the metal (positive) structure.

This displacement of the electron ‘gas’ produces a field and, thus, a restoring force. Using Gauss’ law and the divergence theorem, the field of this symmetric situation may be found as follows.

$$\iiint \nabla \cdot \mathbf{D} dv = \iint \mathbf{D} \cdot d\mathbf{S} = \iiint \rho dv \quad (23)$$

$$\iint \mathbf{D} \cdot d\mathbf{S} = -A \varepsilon_0 E = -NeA\xi \quad (24)$$

All the terms in (24) have been defined except for  $A$ , which is the area of the displacement (not shown in Figure 5). The result of (24) is the restoring field,  $E$ , produced by the displacement of the electron ‘gas.’

$$E = \frac{Ne\xi}{\varepsilon_0} \quad (25)$$

The restoring force may be related to the distance from equilibrium,  $\xi$ , by the following differential equation.

$$F = ma = -eE = -\frac{Ne^2}{\varepsilon_0} \xi(t) = m_e \frac{d^2 \xi(t)}{dt^2} \quad (26)$$

Rewriting (26) yields:

$$\frac{d^2 \xi(t)}{dt^2} + \frac{Ne^2}{m_e \varepsilon_0} \xi(t) = 0. \quad (27)$$

This result is an expression of harmonic motion with a frequency of:

$$\omega_{\text{harmonic}} = \left( \frac{N e^2}{m_e \epsilon_0} \right)^{1/2} = \omega_p. \quad (28)$$

But this is simply the plasma frequency already noted in (9). The polarization in this case, as can be seen from Figure 5, is opposite to the direction of the electric field and corresponds to a relative dielectric constant of zero [1].

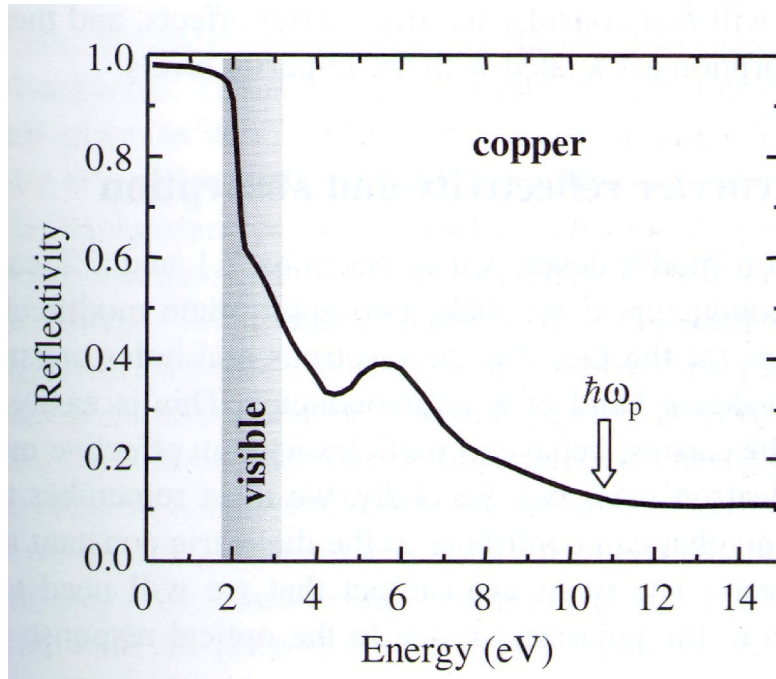
Since the plasma frequency is fairly high for metals, these plasmons can only occur at optical frequencies (UV, typically). Additionally, since the only restriction on plasmons is that they oscillate at an angular frequency of  $\omega_p$ , the wavelength (and thus the speed) of the plasmon can take on any value. Although plasmons are an intriguing phenomenon, they are generally undesirable, and steps must be taken to limit them [3].

### III D. Shortcomings of the Drude Model

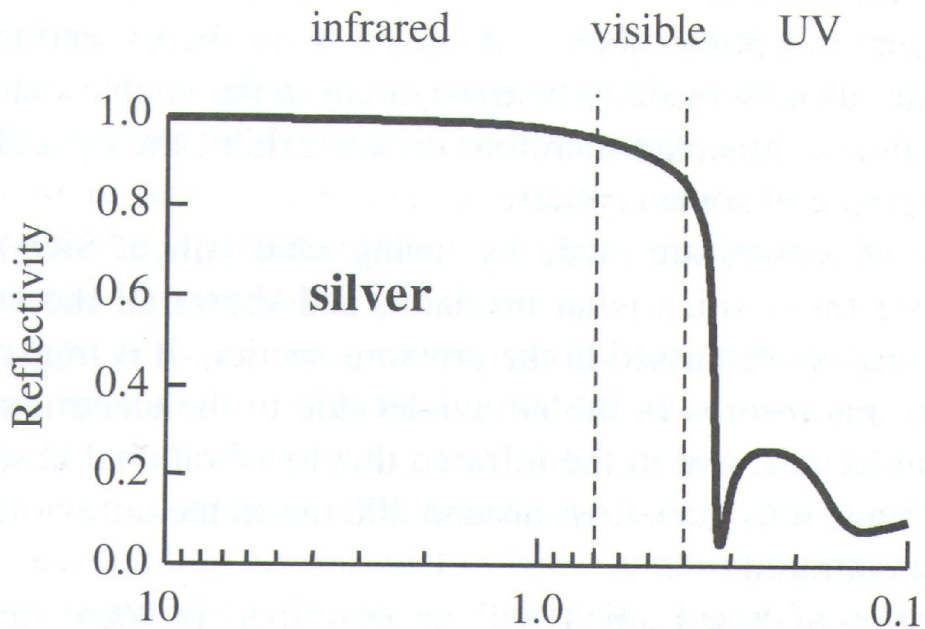
In spite of the fact that the Drude model is reasonably good at predicting some of the characteristics of metals at optical frequencies, it fails miserably for other phenomena. As mentioned earlier, some metals, such as gold and copper, have characteristic colors that cannot be accounted for by the Drude model alone. Figure 6 shows the reflectivity of copper versus the energy of the incident electromagnetic radiation (which is expressed in electron-volts (eV) as  $\hbar\omega$ , where  $\hbar$  is Planck's constant divided by  $2\pi$ ).

As can be seen in Figure 6, the sharp drop in reflectivity from nearly unity does not occur near the plasma frequency but at much lower frequency (energy). In fact, a pronounced drop occurs in the visible region of the spectrum, indicating that reddish colors are reflected while yellows and blues tend to be more highly absorbed. This means that metallic copper has a reddish color.

On the other hand, silver shows the same drop in reflectivity at much lower frequencies than  $\omega_p$ , but this occurs in the UV portion of the spectrum. As a result, silver makes a good substance for mirrors or reflectors. This can be seen in Figure 7, where the plasma wavelength is approximately  $0.14\mu\text{m}$ .



**Figure 6.** The reflection coefficient of copper versus incident electromagnetic energy. (Figure from [1].)



**Figure 7.** The reflection coefficient of silver versus wavelength in  $\mu\text{m}$ . (Figure from [1].)

Although, as predicted by the Drude model, metals ultimately become transparent at higher (UV) frequencies, they are not transparent, necessarily, at all frequencies for which the reflectivity is less than unity. For example, although the reflectivity of copper drops in the visible spectrum, copper is not a transparent material in this region. This

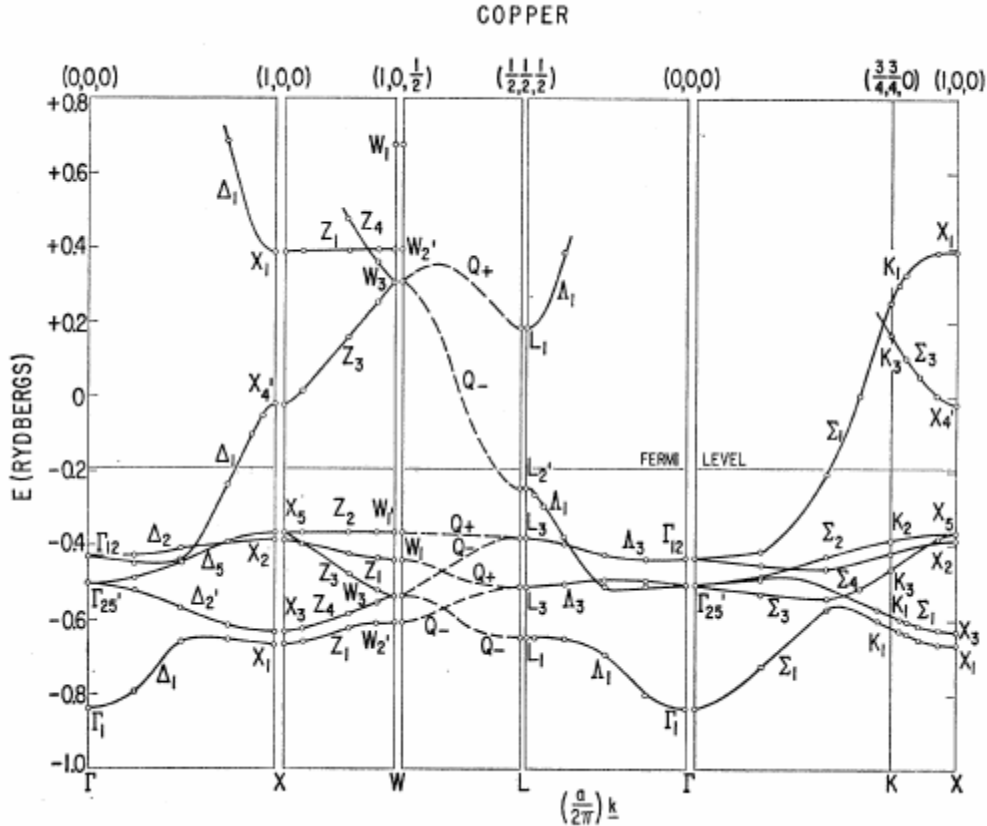
implies that absorption is taking place, a phenomenon that cannot be explained based on the simple assumptions of the Drude model discussed thus far.

Although other phenomena such as electronic heat capacity and the Hall effect are beyond the scope of this paper, the Drude model also fails in accurately predicting these aspects of metal behavior. [4] This may or may not be applicable to specifically optical frequencies, but it further illustrates the need for a more refined model of metals.

#### **IV. Quantum Mechanics and the Band Structure of Metals**

In order to more fully understand the behavior of metals at optical frequencies, specifically the absorption spectrum, a much more thorough examination of the actual structure of the material must be undertaken. Quantum mechanics provides a theoretical model of matter at the sub-atomic level and a much more useful picture of metals (and other materials). A thorough examination of this subject is far beyond the scope of this paper, but it is noteworthy that there is a more accurate model of metals available. Some of the highlights of the application of this theory to metals will be mentioned.

First, the quantum mechanical model of the material involves elimination of the assumption that electrons and positive ions do not interact; in fact, they do interact, thus producing the complicated “band structure” of the material. This band structure predicts at what energies electrons may reside. These energy levels are discrete, and therefore the potential energy level transitions for electrons are quantized. As a result, absorption may only occur at certain frequencies or certain narrow bands of frequencies, which phenomenon may appear in the reflectivity plot as a sharp dip. This is seen for silver at around  $0.3\mu\text{m}$ , as depicted in Figure 7. Figure 8 shows the band structure for copper.



**Figure 8.** The energy band structure of copper. The horizontal axis involves high-symmetry points in the Brillouin zone, labeled using group theory notation. (Figure from [5].)

As can be seen in Figure 8, energy band structures are not trivial matters. However, in order to get a better sense of what might actually be occurring with the reflectivity of metals, and the reasons why the Drude model is not entirely accurate, these sorts of calculations must be made.

Much work has been done, experimentally and theoretically, in determining the band structure of metals and the inter- and intra-band transitions that yield the absorption spectra for incident radiation. This has been done, for example, for silver [5,6], copper [5,7], sodium [8], potassium, rubidium [9], and other pure metals and alloys [10-13].

## V. Summary

A cursory overview of the behavior of metals at optical frequencies, centering primarily on the Drude model, has been presented. Some of the failures of the Drude model were noted and accounted for very lightly using the more complicated quantum mechanical theory of metals. Due to the complexity of quantum mechanics, little was

said, but the theory provides a more rigorous method for dealing with the response of metals to high-frequency incident radiation.

The references cited throughout the discussion provide a number of useful overviews of this matter as well as more specific topical discussions involving particular metals. Some experimental results and theoretical methods for predicting metal behavior are therein reviewed.

## References

- [1] M. Fox, *Optical Properties of Solids*, Oxford University Press, New York, 2001.
- [2] M. Born and E. Wolf, *Principles of Optics, Third (Revised) Ed.*, Pergamon Press, Inc., New York, 1965.
- [3] L. Solymar and D. Walsh, *Lectures on the Electrical Properties of Materials, 3rd Ed.*, Oxford University Press, New York, 1984.
- [4] J. Singleton, *Band Theory and Electronic Properties of Solids*, Oxford University Press, New York, 2001.
- [5] H. Ehrenreich and H.R. Philipp, "Optical properties of Ag and Cu," *Physical Review, Vol. 128, No. 4*, November 15, 1962.
- [6] E.A. Taft and H.R. Philipp, "Optical constants of silver," *Physical Review, Vol. 121, No. 4*, February 15, 1961.
- [7] B.R. Cooper and H. Ehrenreich, "Optical properties of noble metals," *Physical Review, Vol. 138, No. 2A*, April 19, 1965.
- [8] A.J. Sievers, "Infrared and optical properties of sodium metal," *Physical Review Letters, Vol. 45, No 5*, August 4, 1980.
- [9] A.J. Sievers, "Infrared and optical properties of Na, K and Rb metals," *Physical Review B, Vol. 22, No. 4*, August 15, 1980.
- [10] H. Ehrenreich, H.R. Philipp and D.J. Olechna, "Optical properties and Fermi surface of nickel," *Physical Review, Vol. 131, No. 6*, September 15, 1963.
- [11] M. Suffczynski, "Optical constants of metals," *Physical Review, Vol. 117, No. 3*, February 1, 1960.

[12] M. Thèye, "Investigation of the optical properties of Au by means of thin semitransparent films," *Physical Review B*, Vol. 2, No. 8, October 15, 1970.

[13] R.J. Nastasi-Andrews and R.E. Hummel, "Optical properties and electronic structure of dilute Cu-Au, Cu-Zn, Cu-Al, Cu-Ga, Cu-Si, Cu-Ge, Cu-Sn and Cu-As alloys," *Physical Review B*, Vol. 16, No. 10, November 15, 1977.