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7/25/68

A QUANTUM INTERPRETATION OF THE THERMAL
RADIATION PROPERTIES OF METALS

A THESIS

Presented to

The Faculty of the Graduate Division

by

Michael Conlen Noland

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Mechanical Engineering

Georgia Institute of Technology

June, 1970

A QUANTUM INTERPRETATION OF THE THERMAL
RADIATION PROPERTIES OF METALS

Approved:

Chairman

Date approved by Chairman: 51

ACKNOWLEDGMENTS

The author gratefully acknowledges the counsel, assistance and encouragement provided by Dr. S. P. Kezios, the continual interest of Mr. H. L. Stout and Mr. Vern Hopkins, and the silent confidence exhibited by Karen, Kelly and Kristopher.

NOMENCLATURE

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
\vec{A}	Electromagnetic vector potential	statvolt
A_n	Normal component of incident wave	statvolt cm. ⁻¹
A_p	Parallel component of incident wave	statvolt cm. ⁻¹
a_k	Perturbation expansion coefficient	dimensionless
a_q	Phonon creation operator	dimensionless
a_q^+	Phonon creation operator	dimensionless
\vec{B}	Magnetic induction vector	dyne statamp. ⁻¹ cm. ⁻¹
C_e	Constant defined by Eq. (128)	sec. ⁻¹
C_o	Constant defined by Eq. (117)	sec. ⁻¹
c	Speed of propagation of light in vacuum (2.997902 x 10 ¹⁰)	cm. sec. ⁻¹
\vec{D}	Electric displacement vector	statamp. sec. ⁻¹
E	Energy	erg
\vec{E}	Electric field vector	statvolt cm. ⁻¹
$E_{b\lambda}$	Monochromatic emissive power of a blackbody	erg sec. ⁻¹ micron ⁻¹
E_d	Deformation constant	erg
E_f	Fermi energy	erg
E_q	Phonon energy	erg

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
e	Electric charge	statcoulomb
$F_n(\eta, \zeta)$	Function defined by Eq. (114)	dimensionless
\vec{G}	Wave vector in reciprocal lattice	cm.^{-1}
$G_n(\eta, \zeta)$	Function defined by Eq. (115)	dimensionless
$g(E)$	Fermi function	dimensionless
H	Hamiltonian operator	erg
\vec{H}	Magnetic field vector	statamp. cm.^{-1}
H'	Perturbation Hamiltonian	erg
H°	Zero-order Hamiltonian	erg
\mathcal{H}	Classical Hamiltonian	erg
h	Planck's constant (6.6256×10^{-27})	erg sec.
\hbar	$h/2\pi$ (1.0542×10^{-27})	erg sec.
\vec{J}	Electric current density	statvolt $\text{cm.}^{-1}\text{sec.}^{-1}$
$J(\omega, T)$	Function defined by Eq. (113)	dimensionless
K	Boltzmann constant (1.380257×10^{-16})	erg deg. $^{-1}$
k	Extinction coefficient	dimensionless
\vec{k}	Electron wave vector	cm.^{-1}
L	Lorenz number	erg $\text{cm.}^{-1}\text{deg.}^{-2}$
M	Mass of ion	gm.
m	Mass of electron	gm.
m^*	Effective electron mass	gm.
N	Number of electrons per unit volume	cm.^{-3}

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
N_p	Number of phonons per unit volume	cm.^{-3}
n	Index of refraction	dimensionless
\bar{n}	Complex index of refraction	dimensionless
\bar{n}_i	Complex index of refraction, ideal metal	dimensionless
n_q	Number of phonons in state \vec{q}	dimensionless
P_r^s	Electron transition probability	sec.^{-1}
\vec{p}	Photon wave vector	cm.^{-1}
\hat{p}	Quantum momentum operator	erg sec. cm.^{-1}
$Q(\eta, \zeta)$	Quantum correction factor	dimensionless
\vec{q}	Phonon wave vector	cm.^{-1}
R_n	Normal component of reflected wave	statvolt cm.^{-1}
R_p	Parallel component of reflected wave	statvolt cm.^{-1}
\vec{r}	Position vector	cm.
S_e	Electron-electron collision cross-section	cm.^2
T	Temperature	$^{\circ}\text{K}$
t	Time	sec.
$V(\vec{r})$	Interaction potential	erg
$V_d(\vec{r}, t)$	Deformation potential	erg
v_f	Electron velocity at the Fermi level	cm. sec.^{-1}
W	Power expenditure of electromagnetic field	erg sec.^{-1}
α	Absorptivity	dimensionless

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
α_λ	Monochromatic absorptivity	dimensionless
α'	Polarizability	cm. ³
α_b	Bulk absorptivity	dimensionless
α_s	Skin absorptivity	dimensionless
Γ	Electron-phonon damping coefficient	sec. ⁻¹
Γ_e	Electron-electron damping coefficient	sec. ⁻¹
Γ_i	Electron-impurity damping coefficient	sec. ⁻¹
Γ^0	dc damping coefficient	sec. ⁻¹
γ	Angle between \vec{k} and \vec{q}	radian
δ_{mn}	Kronecker delta	dimensionless
$\delta(x)$	Dirac delta function	dimensionless
ϵ	Emissivity	dimensionless
ϵ_λ	Monochromatic emissivity	dimensionless
$\bar{\epsilon}$	Dielectric constant	dimensionless
$\bar{\epsilon}$	Complex dielectric constant	dimensionless
ζ	Function defined by Eq. (116)	dimensionless
η	Function defined by Eq. (116)	dimensionless
θ	Debye temperature	°K
κ	Thermal conductivity	erg cm. ⁻¹ sec. ⁻¹ deg. ⁻¹
μ	Permeability	dyne statamp. ⁻²
ν	Frequency	sec. ⁻¹
ρ	Reflectivity	dimensionless

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
ρ_λ	Monochromatic reflectivity	dimensionless
ρ_0	Residual resistivity	sec.
ρ_p	Phonon density	gm. cm. ⁻³
σ	Electrical conductivity	sec. ⁻¹
σ_0	dc conductivity	sec. ⁻¹
Φ	Electromagnetic scalar potential	statvolt
χ	Magnetic susceptibility	dimensionless
Ψ	Wave function	dimensionless
Ψ^0	Zero-order wave function	dimensionless
Ω	Solid angle	steradian
ω	Angular frequency	sec. ⁻¹
ω_{mn}	Bohr frequency	sec. ⁻¹
ω_p	Plasma frequency	sec. ⁻¹
ω_q	Phonon angular frequency	sec. ⁻¹

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SUMMARY

The thermal design of equipment and processes in which thermal radiation is an important mode of heat transfer demands an adequate knowledge of the thermal radiation properties of materials. The research described in this thesis is directed toward the application of quantum concepts to an interpretation of the physical basis of the thermal radiation properties of metals. Emphasis is placed on the development of theoretical relations which can be used in the routine correlation and prediction of these properties.

A simplified model of the atomic system is proposed in which it is assumed that absorption and emission in metals are the result of second-order processes involving simultaneous electron-photon and electron-phonon interactions. A perturbation solution of the Schrodinger equation is obtained and the second-order transition probabilities are computed from which the energy expenditure of the field is determined. The results can be interpreted in terms of an electron-phonon damping coefficient which is added to damping terms which account for electron-electron and electron-impurity interactions. The bulk absorptivity is obtained when the total damping coefficient is used in the dispersion relations. The result explicitly indicates the temperature-dependence and frequency-dependence of the normal monochromatic emissivity.

CHAPTER I

INTRODUCTION

The expansion of aerospace technology during the past decade has stimulated interest and activity in the field of radiation energy exchange between solids and their environment. Heat transfer by radiation is the principal thermodynamic process by which spacecraft maintain thermal balance. It is also an important mode of energy transfer for high-velocity bodies entering a planetary atmosphere. However, interest in thermal radiation is no longer confined to aerospace and military hardware systems. The demand for new processes and materials has led to numerous industrial systems in which operating temperatures are sufficiently high that radiation becomes an important mode of heat transfer.

The design of equipment in which thermal radiation is important usually involves the calculation of the net radiative heat transfer between various points in the system or between the system and its environment. Knowledge of the thermal radiation properties of surfaces is basic to any such analysis. The accuracy of even the most sophisticated analysis ultimately depends on the accuracy with which the thermal radiation properties are known. The choice of a mathematical technique to solve the often complicated equations of radiative transfer is of little concern if only crude estimates of the surface properties are available.

Considerable effort has been devoted to the experimental determination of the emittance, absorptance, reflectance and transmittance of various solids and fluids under a wide variety of test conditions. However, the theoretical aspects of thermal radiation properties have received only limited attention. Very few researchers in the engineering sciences have addressed themselves to the fundamental question of the nature of the physical phenomena which arise when a thermal radiation field interacts with matter. The research described in this thesis is directed toward the investigation of the physical principles which underly the phenomena manifested by the thermal radiation properties of solids. Emphasis is placed on the use of quantum mechanics to explain and correlate the wavelength and temperature dependence of the emissivity with particular attention devoted to the importance of thermal lattice vibrations. Although much of the theory is applicable to all solids, the final theoretical expressions are developed only for electrically conductive solids, i.e. metals.

Thermal Radiation Properties of Opaque Solids

The thermal radiation properties of a solid characterize the degree to which that solid can exchange energy with a thermal radiation field. These properties appear in an energy balance for an element of area on the surface of a solid which is exchanging energy by radiation with its surroundings. Their definitions and phenomenological nature

have been extensively treated in the literature (1,2). We shall adopt the terminology convention in which terms such as emissivity, absorptivity and reflectivity refer to properties of a material whereas terms such as emittance, absorptance and reflectance refer to the property of a particular specimen (3). Accordingly, emissivity, for example, is a property of an ideal specimen which is homogenous, chemically clean and has surfaces with a roughness much smaller than the wavelength of the incident radiation field. It is a characteristic of the material independent of the size or shape of the specimen. Experimental measurements yield values of the emittance which depend on the conditions of the specimen surface. For specimens which are very clean and have nearly optically smooth surfaces, the measured emittance approaches the emissivity.

The present research is concerned with the emissivity ϵ of opaque, electrically-conductive solids. In many engineering applications it is assumed that Kirchhoff's law applies in such a manner that the emissivity and the absorptivity α are equal,

$$\alpha = \epsilon \quad (1)$$

This is never exactly valid for a system in which there is non-zero heat transfer; nevertheless, it is nearly always assumed to be true for engineering calculations.

The absorptivity and reflectivity are related by the conservation of energy,

$$\alpha + \rho = 1 \quad (2)$$

The relations expressed in Eqs. (1) and (2) allow a radiative heat transfer analysis to be carried out when values of only one of the radiation properties are known. The same relations hold for monochromatic radiation properties, i.e.,

$$1 - \rho_\lambda = \alpha_\lambda = \epsilon_\lambda \quad (3)$$

The total emissivity is related to the monochromatic emissivity by definition,

$$\epsilon = \frac{\int_0^\infty \epsilon_\lambda E_{b\lambda} d\lambda}{\int_0^\infty E_{b\lambda} d\lambda} = \frac{1}{\sigma T^4} \int_0^\infty \epsilon_\lambda E_{b\lambda} d\lambda \quad (4)$$

where $E_{b\lambda}$ is the monochromatic emissive power of a blackbody at temperature T in the same surroundings as the specimen. Thus, for many engineering calculations, it is sufficient to consider only the monochromatic emissivity of the surfaces.

The emittance of a solid surface is a function of several parameters which describe the external radiation field and the nature of the surface:

- (1) The wavelength of the electromagnetic field;
- (2) The state of polarization of the field;
- (3) The temperature of the emitting surface;
- (4) The polar and azimuth angle at which the emission of the surface is observed; and

(5) The physical and chemical condition of the surface. Monochromatic emittance is determined by measuring the intensity and state of polarization of the emitted radiation at a particular wavelength and for a range of surface temperatures in all directions above the surface. This must be accompanied by a complete description of the condition of the specimen surface.

The wavelength and state of polarization of the field and the temperature of the surface are well-defined variables. Similarly, the polar and azimuth angles are defined by the arrangement of the experimental apparatus. However, a lack of adequate description of the surface condition has reduced the usefulness of much of the emittance data reported in the literature. If heat transfer by thermal radiation is critical in an engineering system, it is usually necessary for the designer to conduct measurements of the emittance of the particular surfaces to be employed

in the design. He can use values from the literature only if he has carefully defined the surface conditions and is fortunate enough to find published data for nearly the same surface conditions.

The surface condition of a particular specimen of a given material can be considerably different from that of another specimen of the same material. This can lead to markedly different values of emittance. The problem of surface condition is illustrated in Figure 1 which shows the total normal emittance of coated molybdenum as a function of temperature (4). The inconsistency of the data demonstrates the need for adequate surface specification and also gives an indication of the enormous amount of data which would be required to satisfy the general engineering need.

The relatively large number of variables upon which the emittance depends and the wide variety of possible surface conditions provide an explanation for the fact that experiment is, at present, more advanced than theory in the study of the thermal radiation properties of solids. The need for data has stimulated the development of many experimental methods for the measurement of the emittance or reflectance of various materials over wide temperature ranges. The theory, however, has been neglected. Only a few preliminary attempts have been made to overcome the serious inadequacies of the classical theory of the optical properties of solids first developed by Drude (5). The lack of effort devoted to

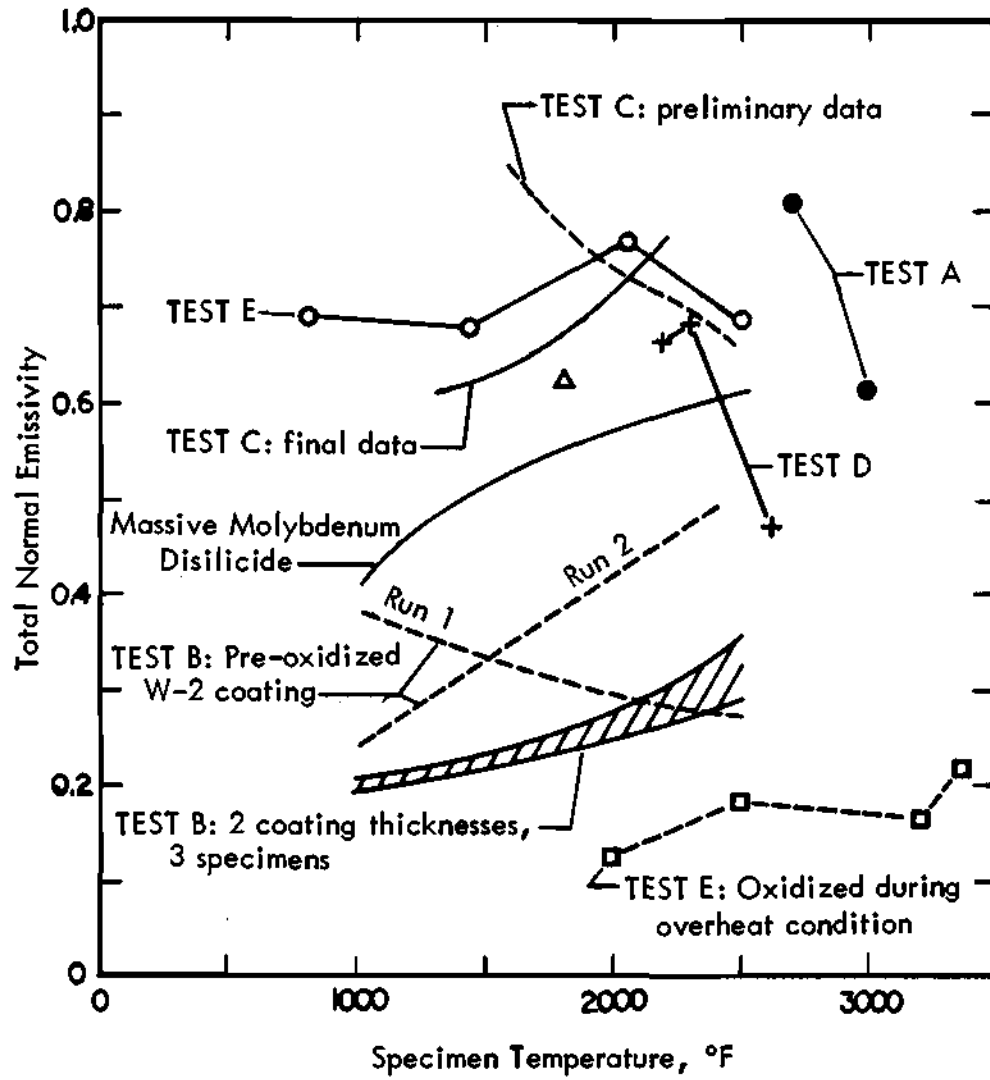


Figure 1. Total Normal Emissivity of W-2 Coated Molybdenum

theory is undoubtedly due in part to the emphasis placed on experimental studies and the difficulties encountered in attempts to develop theoretical models which are useful in engineering analysis and correlation.

The Need for Theoretical Studies

One of the most important incentives for undertaking the theoretical study of the thermal radiation properties of solids is a desire for a better understanding of the fundamental physical phenomena which give rise to these properties. Experimental studies can yield the emittance data required in thermal design; however, unless combined with theory, they provide no insight into what occurs when a thermal radiation field interacts with a solid. As is the case with most phenomenological coefficients, the thermal radiation properties can be utilized in the design of hardware or processes without an understanding of the related physical phenomena. Nonetheless, it is reasonable to expect that a more thorough knowledge of the physics involved would contribute to improved design and analysis methods.

In addition to the intrinsic desirability of an enhanced basic understanding of radiation properties, an additional justification of theoretical studies is their use to interpolate and extrapolate property data originally obtained over relatively short wavelength and temperature ranges. For example, an adequate theory could be used to prepare high-temperature monochromatic emissivity curves when only room-temperature experimental

data were available, thereby eliminating, in some cases, the necessity for high-temperature measurements. Empirical relations could be used for the same purpose; however, the temperature coefficient of monochromatic emissivity is a function of wavelength for most metals, as shown in Figure 2. Therefore, it would require a considerable amount of experimental data to generate empirical relations. The availability of such data would reduce the value of the resulting relations.

The utilization of theory in the development and evaluation of experimental apparatus and methods is another reason for conducting theoretical studies of the thermal radiation properties of solids. Also, an accurate theory, which would necessarily be based upon the atomic nature of the material, could conceivably be applied to the formulation of materials with specifically designed and controlled thermal radiation characteristics. This latter application is well beyond the extent of the theory described in this thesis. Hopefully, however, the present theory might indicate the directions to be taken in a more complete analysis.

Wave Propagation in a Conducting Medium

Energy exchange by thermal radiation is an electromagnetic wave phenomenon and is thus closely related to the phenomena described in physical optics. Energy is transported through space in the form of an electromagnetic field. When the field encounters an atomic system, such as a solid, it interacts with this system. Energy can be reflected or absorbed

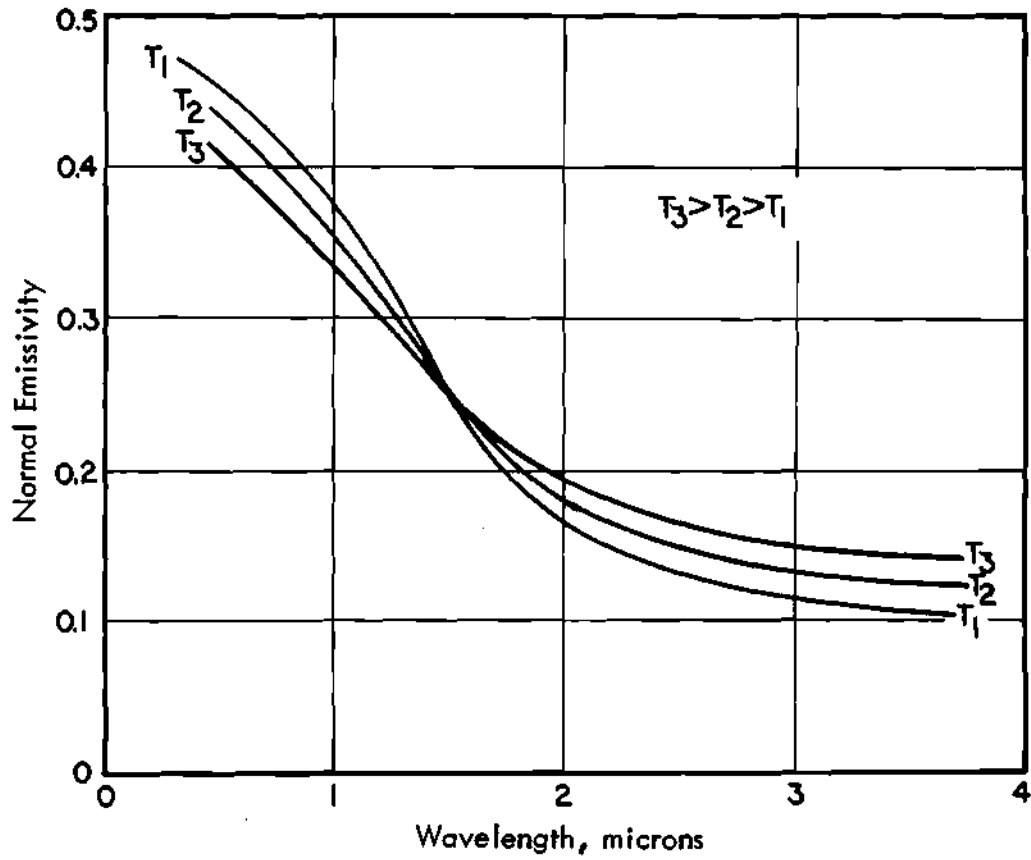


Figure 2. Normal Monochromatic Emissivity of a Typical Refractory Metal

by the system or transmitted through it. If the atoms or molecules absorb energy and are thereby excited to higher energy levels, they can emit energy into the radiation field. It is this multi-faceted interaction between electromagnetic radiation and matter which gives rise to the thermal radiation properties.

The nature of the thermal radiation properties depends on whether the material is a conductor or a dielectric. The research described herein is limited to the study of the characteristics of conducting solids, i.e. metals. We are thus concerned with the manner in which electromagnetic radiation propagates in a conducting medium. A metal with finite electrical conductivity will exhibit Joulean heating when subjected to an electromagnetic field. Such heating is an irreversible thermodynamic process; hence, the field is attenuated as it penetrates the metal and energy is absorbed. Because of their high electrical conductivity, metals exhibit strong absorption and require only a small thickness to be essentially opaque.

The thermal radiation characteristics of homogeneous materials with smooth surfaces can be computed if the optical constants n and k are known as functions of temperature and wavelength. The single exception to this is the case of metals at low temperatures where the anomalous skin effect becomes important. The index of refraction n and the extinction coefficient k constitute the real and imaginary parts, respectively, of the complex index of refraction of a metal,

$$\bar{n} = n - ik \quad (5)$$

This parameter appears in a macroscopic analysis of the propagation of a wave through a conducting medium. We shall therefore commence our analysis with a brief review of this phenomena.

When an electromagnetic field is incident on a metal the resulting macroscopic phenomena can be described with the aid of the classical Maxwell field equations. If the metal is characterized by a conductivity σ , a dielectric constant $\tilde{\epsilon}$ and a permeability μ , the Maxwell equations are (6)

$$\nabla \times \vec{H} = \frac{\tilde{\epsilon}}{c} \frac{\partial \vec{E}}{\partial t} + \frac{4\pi}{c} \sigma \vec{E} \quad (6)$$

$$\nabla \times \vec{E} = - \frac{\mu}{c} \frac{\partial \vec{H}}{\partial t} \quad (7)$$

$$\nabla \cdot \vec{E} = 0 \quad (8)$$

$$\nabla \cdot \vec{H} = 0 \quad (9)$$

where \vec{E} is the electric field vector, \vec{H} is the magnetic field vector and c is the speed of light in vacuum. To maintain consistency with the pertinent literature in the field of optics, the Gaussian system of units

shall be employed. Thus the electrical quantities will be represented in electrostatic units and the magnetic quantities in electromagnetic units. Elimination of the magnetic field vector from Eqs. (6) and (7) yields the equation for a damped wave,

$$\nabla^2 \vec{E} = \frac{\mu \tilde{\epsilon}}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi\mu\sigma}{c^2} \frac{\partial \vec{E}}{\partial t} \quad (10)$$

Similarly, the magnetic field vector also satisfies the wave equation,

$$\nabla^2 \vec{H} = \frac{\mu \tilde{\epsilon}}{c^2} \frac{\partial^2 \vec{H}}{\partial t^2} + \frac{4\pi\mu\sigma}{c^2} \frac{\partial \vec{H}}{\partial t} \quad (11)$$

If the field is monochromatic with angular frequency ω , the field vectors can be written as $\vec{E} = \vec{E}_0 e^{-i\omega t}$ and $\vec{H} = \vec{H}_0 e^{-i\omega t}$. The differential operators then become $\partial/\partial t = -i\omega$ and $\partial^2/\partial t^2 = -\omega^2$ and Eq. (10) becomes

$$\nabla^2 \vec{E} = \frac{\mu\omega^2}{c^2} \left(\tilde{\epsilon} + i \frac{4\pi\sigma}{\omega} \right) \vec{E} \quad (12)$$

If we define a complex dielectric constant as

$$\bar{\epsilon} = \tilde{\epsilon} + i \frac{4\pi\sigma}{\omega} \quad (13)$$

then Eq. (12) is of the same mathematical form as the corresponding equation for dielectric media (7). In a non-conducting material the dielectric constant is equal to the square of the index of refraction. Hence, the formal analogy between conductors and dielectrics can be extended by defining a complex index of refraction for conducting materials,

$$\bar{n}^2 = (n-ik)^2 = \bar{\epsilon} \quad (14)$$

The permeability is defined in terms of the magnetic susceptibility χ as

$$\mu = 1 + 4\pi\chi \quad (15)$$

For metals, throughout the visible and infrared portions of the spectrum, χ is of the order 10^{-6} . Thus, to a high degree of accuracy, we can approximate μ by one dyne statamp.⁻² for metals (6).

The real and imaginary parts of the complex index of refraction, i.e. the refractive index and the extinction coefficient, are given in terms of the real and imaginary parts of

$$\bar{n}^2 = n^2 - 2ink - k^2 = \epsilon + \frac{i4\pi\sigma}{\omega} \quad (16)$$

which yields

$$n^2 = \frac{1}{2} \left[\left\{ \epsilon^2 + \left(\frac{4\pi\sigma}{\omega} \right)^2 \right\}^{1/2} + \epsilon \right] \quad (17)$$

$$k^2 = \frac{1}{2} \left[\left\{ \epsilon^2 + \left(\frac{4\pi\sigma}{\omega} \right)^2 \right\}^{1/2} - \epsilon \right] \quad (18)$$

Hence, the optical properties of metals can be expressed in terms of the dielectric constant and the conductivity, both of which must be regarded as functions of frequency and temperature. These parameters are phenomenological coefficients which are defined by the constitutive relations $\vec{J} = \sigma \vec{E}$ and $\vec{D} = \epsilon \vec{E}$ where \vec{J} is the electric current density and \vec{D} is the electric displacement vector. Relations for the optical properties which are based on Maxwell's equations are valid regardless of the details of the atomic system. The latter enter only into attempts to relate σ and ϵ to the atomic parameters of the absorbing medium. Thus, although we might expect quantum effects to be important in the frequency and temperature dependence of σ and ϵ , we shall treat Eqs. (17) and (18) as independent of the particular choice of an atomic model. Before proceeding to the development of the atomic theory, however, it is necessary to state the relations between the optical properties of metals and their thermal radiation properties.

Reflection and Refraction at a Metallic Surface

When an electromagnetic field is incident on the surface of an opaque body a fraction of the energy is reflected and the remainder is absorbed. The emissivity and absorptivity of the body can be obtained from the reflectivity using Eq. (3). We have seen that the equation of propagation of a wave through a conductor is formally identical to that for a dielectric if we introduce a complex index of refraction. Thus the expressions which describe reflection and refraction at a surface are also the same if we use the complex index of refraction for metals. These expressions are the Fresnel equations (6). Consider the case of a wave propagating through a medium of refractive index n_1 and incident on the surface of a metal with complex index of refraction \bar{n} . Let A be the amplitude of the electric vector of the field. We resolve A into a component A_p parallel to the plane of incidence and a component A_n normal to the plane of incidence. The Fresnel equations are then

$$R_p = \frac{\bar{n} \cos \theta - n_1 \cos \alpha}{\bar{n} \cos \theta + n_1 \cos \alpha} A_p \quad (19)$$

$$R_n = \frac{n_1 \cos \theta - \bar{n} \cos \alpha}{n_1 \cos \theta + \bar{n} \cos \alpha} A_n \quad (20)$$

where R_p and R_n are the components of the amplitude of the reflected wave and θ and α are the angles of incidence and refraction, respectively, measured from the normal, as shown in Figure 3. The reflectivity is defined as the ratio of the reflected energy to the incident energy. The energy of a wave is proportional to the square of the absolute value of the amplitude; hence

$$\rho = \frac{|R|^2}{|A|^2} \quad ; \quad \rho_p = \frac{|R_p|^2}{|A_p|^2} \quad ; \quad \rho_n = \frac{|R_n|^2}{|A_n|^2}$$

or

$$\rho_p = \left| \frac{\bar{n} \cos \theta - n_1 \cos \alpha}{\bar{n} \cos \theta + n_1 \cos \alpha} \right|^2 \quad (21)$$

$$\rho_n = \left| \frac{n_1 \cos \theta - \bar{n} \cos \alpha}{n_1 \cos \theta + \bar{n} \cos \alpha} \right|^2 \quad (22)$$

For the case of a wave incident normal to the surface from free space

($n_1 = 1$) the normal reflectivity is

$$\rho = \rho_p = \rho_n = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (23)$$

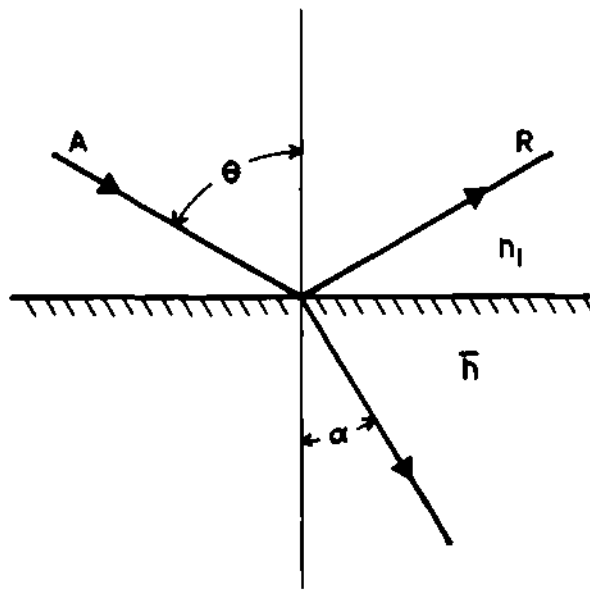


Figure 3. Geometry of Reflection and Refraction

The optical constants n and k are functions of frequency and temperature. Therefore the reflectivity also depends on the frequency of the field and the temperature of the solid. The normal monochromatic emissivity follows from Eqs. (3) and (23),

$$\epsilon_n(\omega, T) = 1 - \rho_n(\omega, T) = \frac{4n}{(n+1)^2 + k^2} \quad (24)$$

The relation given in Eq. (24) provides a means to calculate the normal monochromatic emissivity if n and k are known as functions of frequency and temperature. In order to obtain the necessary relations, some form of atomic or microscopic model must be devised. The conductivity and dielectric constant of a metal appear in the wave propagation equations and indicate that the wave is attenuated as it propagates in the metal. This means that the atomic system of the metal absorbs energy from the incident field. The analysis of this absorption is a two-fold task: first, a suitable atomic model must be devised and, secondly, the laws of physics must be used to analyze the exchange of energy between this atomic system and the electromagnetic field. Initial attempts to explain the optical properties utilized the laws of classical physics. While the resulting theory contributed a great deal to our understanding of metals, we now recognize the fact that quantum physics is required to explain many of the observed phenomena. The research described in this

thesis is based on quantum-mechanical relations. The classical theory, however, provides an essential introduction to the atomic concept and, therefore, is presented in the next chapter.

CHAPTER II

A REVIEW OF THE CLASSICAL THEORY
OF THE OPTICAL PROPERTIES OF METALS

In the previous chapter we have noted that the thermal radiation properties of metals can be expressed in terms of the optical properties n and k which, in turn, can be expressed as functions of the conductivity and the dielectric constant. Experiment shows that the so-called optical "constants" are dispersive, i.e. they are functions of frequency. Furthermore, they vary with the temperature of the metal. These observations cannot be explained solely in terms of electromagnetic theory. The discontinuous structure of matter must be included in a more detailed microscopic analysis of the interaction between an atomic system and an incident electromagnetic field.

Prior to the advent of quantum mechanics, interest in the microscopic properties of metals centered around attempts to explain their high electrical conductivity when compared to dielectric materials. These attempts involved the development of a mechanical model of the atomic system and the subsequent application of classical mechanics to describe the changes induced in the model by the electrical forces due to an electromagnetic field. The most important of these early theories, and the

one on which much later development and refinement was based, was the free-electron theory of metals proposed by Drude.

The Drude Free-Electron Theory

Considering the stage of development of atomic theory in 1900, the model for metals proposed during that year by Drude (5) demonstrated considerable insight. He suggested that metals can be treated as composed of an array of positively-charged metallic ions through which the valence electrons are free to move. This free-electron gas remains in thermal equilibrium with the ionic array. In the absence of an external electromagnetic field, the motion of each electron is random. When an electric field is imposed, the electrons are accelerated in the positive field direction. This directed acceleration accounts for the presence of an electric current. If the electrons were free to move, however, they would accelerate indefinitely under the influence of a constant field. This would imply infinite conductivity. To explain the observed finite conductivity of metals, Drude proposed that the valence electrons undergo frequent collisions with the lattice ions and that these collisions result in the loss of the drift momentum of the electrons.

The mathematical formulation of the Drude model is obtained by considering the dynamics of a free electron subjected to a damping force which is proportional to the electron velocity and the force due to an electric field. The equation of motion of such an electron is

$$m \frac{\partial^2 \vec{r}}{\partial t^2} + m\Gamma \frac{\partial \vec{r}}{\partial t} = e\vec{E}_0 e^{i\omega t} \quad (25)$$

where m is the electron mass, e is the electron charge, r is the position vector and Γ is a mean damping coefficient. If, according to Drude's hypothesis, the electron drift velocity is lost during collisions, then the average electron acceleration must vanish. For the x-component of motion, for example, the solution of the equation of motion must correspond to $\overline{\partial^2 x / \partial t^2} = 0$. Thus

$$\overline{\frac{\partial x}{\partial t}} = \frac{eE_x}{m\Gamma} \quad (26)$$

The average velocity is defined in terms of the mean time between collisions, t_0 ,

$$\bar{v}_x = \overline{\frac{\partial x}{\partial t}} = \frac{1}{t_0} \int_0^{t_0} \frac{\partial x}{\partial t} dt \quad (27)$$

The conduction current density in the x-direction is the product of the electron charge, the number of electrons per unit volume N and the average velocity in the x-direction, i.e.,

$$\sigma_0 E_x = Ne\bar{v}_x = \frac{Ne^2}{m\Gamma} E_x \quad (28)$$

where σ_0 is the dc conductivity corresponding to a constant field with zero frequency. Thus, the mean damping coefficient is

$$\Gamma = \frac{Ne^2}{m\sigma_0} \quad (29)$$

The current due to the motion of charged carriers is the sum of the polarization current $\alpha'(\partial\vec{E}/\partial t)$ and the conduction current $\sigma\vec{E}$ (8),

$$\vec{J} = \alpha' \frac{\partial\vec{E}}{\partial t} + \sigma\vec{E} \quad (30)$$

where α' is the polarizability of the medium related to the real dielectric constant by $\epsilon' = 1 + 4\pi\alpha'$. Since $\vec{E} = \vec{E}_0 e^{i\omega t}$ then $\partial\vec{E}/\partial t = i\omega\vec{E}$ and

$$\vec{J} = (\sigma + i\omega\alpha')\vec{E} \quad (31)$$

For sufficiently long periods of time, the solution of Eq. (25) is

$$\vec{r} = \frac{e/m}{-\omega^2 + i\Gamma\omega} \vec{E}_0 e^{i\omega t} \quad (32)$$

Thus

$$\vec{J} = Ne \frac{\partial \vec{r}}{\partial t} = (\sigma + i\omega\alpha') \vec{E} = N \frac{e^2}{m} \frac{i\omega}{(-\omega^2 + i\Gamma\omega)} \vec{E}_0 e^{i\omega t} \quad (33)$$

Equating real and imaginary parts and noting that $\alpha' = (\tilde{\epsilon} - 1)/4\pi$,
we have

$$\sigma = \frac{Ne^2}{m} \left(\frac{\Gamma}{\omega^2 + \Gamma^2} \right) \quad (34)$$

$$\tilde{\epsilon} = 1 - \frac{4\pi Ne^2}{m} \left(\frac{1}{\omega^2 + \Gamma^2} \right) \quad (35)$$

From Eq. (34), when $\omega = 0$ the dc conductivity is

$$\sigma_0 = \frac{Ne^2}{m\Gamma} \quad (36)$$

Thus Eqs. (34) and (35) can be written

$$\sigma = \sigma_0 \left(\frac{\Gamma^2}{\omega^2 + \Gamma^2} \right) \quad (37)$$

$$\tilde{\epsilon} = 1 - 4\pi\sigma_0 \left(\frac{\Gamma}{\omega^2 + \Gamma^2} \right) \quad (38)$$

The Drude theory treats the damping coefficient as non-dispersive
or, frequency-independent, as can be seen from Eq. (29). The existence

of a non-zero Γ implies that each valence electron can move freely through the lattice for a period of time equal, on the average, to $1/\Gamma$. It then undergoes a collision with an ion which absorbs all of the energy which has been gained by the electron due to the incident electromagnetic field. In a hypothetical ideal metal in which the valence electrons do not interact with the lattice the damping coefficient is zero. The square of the complex index of refraction of such a metal is real and

$$\bar{n}_1^2 = \bar{\epsilon} = \bar{\epsilon}' = 1 - \frac{4\pi Ne^2}{m\omega^2} \quad (39)$$

For high frequencies the refractive index of an ideal metal is not only real but also less than unity corresponding to a condition of transparency. For frequencies sufficiently small that $4\pi Ne^2/m\omega^2$ is greater than unity, the refractive index is imaginary and total reflection occurs. The second term in Eq. (39) is seen to contain the plasma frequency of a free-electron gas (9)

$$\omega_p = \left(\frac{4\pi Ne^2}{m} \right)^{1/2} \quad (40)$$

In the case of a real metal, the behavior of the optical constants depends on the relative magnitudes of the frequency and the damping coefficient. If $\Gamma \gg \omega$, as might occur in the far infrared, the relations

given by the Drude theory can be approximated by

$$\sigma = \frac{Ne^2}{m\Gamma} \approx \sigma_0$$

and

$$\bar{\epsilon} = 1 - \frac{4\pi Ne^2}{m\Gamma^2}$$

Then, from Eqs. (17) and (18),

$$n^2 \approx \frac{2\pi Ne^2}{m\Gamma^2} \left\{ \left[\frac{\Gamma^2}{\omega^2} + 1 \right]^{1/2} - 1 \right\} \approx \frac{2\pi Ne^2}{m\Gamma\omega} \quad (41)$$

$$k^2 \approx \frac{2\pi Ne^2}{m\Gamma^2} \left\{ \left[\frac{\Gamma^2}{\omega^2} + 1 \right]^{1/2} + 1 \right\} \approx \frac{2\pi Ne^2}{m\Gamma\omega} \quad (42)$$

Hence, if $\Gamma \gg \omega$,

$$n = k = \left(\frac{2\pi Ne^2}{m\Gamma\omega} \right)^{1/2} = \left(\frac{2\pi\sigma_0}{\omega} \right)^{1/2} = \left(\frac{\sigma_0}{\nu} \right)^{1/2} \quad (43)$$

were $\nu = \omega/2\pi$. It follows from Eq. (23) that

$$\rho \approx \frac{(n-1)^2 + n^2}{(n+1)^2 + n^2} = 1 - \frac{2}{n} + \frac{2}{n^2} - \frac{1}{n^3} + \frac{1}{2n^5} - \frac{1}{2n^6} + \dots$$

Then the normal monochromatic emissivity is

$$\epsilon_n = 1 - \rho \approx 2 \sqrt{\frac{\nu}{\sigma_0}} - 2 \frac{\nu}{\sigma_0} + \left(\frac{\nu}{\sigma_0}\right)^{3/2} - \dots \quad (44)$$

This is the familiar Hagen-Rubens formula (10), the only expression which has been used to any appreciable extent in correlating and analyzing thermal radiation property data. It represents a low-frequency approximation of the Drude free-electron theory. Usually only the first one or two terms are retained.

The Hagen-Rubens formula has been used as the basis for the derivation of several other emissivity relations. Aschkinass (11) obtained an equation for the temperature-dependent normal emissivity by combining the first term in the Hagen-Rubens formula with an integration over the Planck distribution using a linear temperature dependence for the conductivity. Foote (12) derived a similar relation retaining the first two terms of the Hagen-Rubens formula. Davisson and Weeks (13) employed the Fresnel equations to develop an expression for the hemispherical emissivity. This expression was later extended by Schmidt and Eckert (14) who applied graphical integration techniques. More recently Parker and Abbott (15) have developed emissivity relations based on the Drude theory with a constant finite damping coefficient. These various relations have been summarized by Richmond, Dunn, DeWitt and Hayes (16). They are all, however,

limited to an even smaller range of conditions than those under which the original Drude theory is valid since they represent only the low-frequency limit of the classical free-electron theory.

The range of validity of the Drude theory as a means of computing the optical properties of metals has been discussed by Schulz (17) who compared a considerable number of experimental values of n and k with corresponding values predicted by the theory. He found excellent agreement for liquid mercury and gallium over the entire frequency range for which data were available. Correlation was good for silver and gold at wavelengths longer than two microns. The results for copper were also in good agreement for wavelengths longer than two microns if the effective mass of the conduction electrons was taken to be 1.45 times the electron rest mass. Agreement could be obtained for aluminum at long wavelengths if an empirical value of conductivity was used which did not correspond to experimental values.

The Drude theory was extended by Lorentz (18) who applied classical Maxwell-Boltzmann statistics to the electron gas. The potential field of the positive lattice ions was assumed to be constant in space and the electron-electron interaction was neglected. This modification indicated that the resistivity should be proportional to the square root of temperature rather than the observed linear dependence. This discrepancy is due in part to the fact that the electron gas obeys the Fermi-Dirac quantum statistics rather than Maxwell-Boltzmann statistics. The theory of Lorentz

was presented in 1909, almost two decades before the development of the Fermi-Dirac statistics. Although it provided a prediction of the temperature dependence of dc resistivity, it was less satisfactory in predicting optical properties than the simple Drude theory.

The shortcomings of the Drude theory would appear to be related to the inadequacies of the atomic model. It would seem unlikely that the damping coefficient for a real metal is non-dispersive. Furthermore, the classical free-electron theory does not account for the influence of the metal temperature. It is postulated that the electron damping is due to electron-lattice collisions. Such interactions should exhibit a temperature dependence because vibrations of the lattice ions are strongly influenced by temperature. These inadequacies can be overcome only by the development of a quantum theory.

Classical Multi-electron Theory

The original model proposed by Drude included the possibility that two different types of charge carriers might contribute to the optical properties of a metal. At the time, however, this postulate appeared to be inconsistent with the theory of the electron and Drude abandoned it in favor of the single free-electron theory described above. The latter formulation was not adequately tested until the 1950's when its restricted range of validity became apparent. In 1955, Roberts (19), recognizing the similarity between Drude's two types of electrons and the electron and

hole charges which are important in semiconductor physics, revitalized the original Drude hypothesis. In his initial development Roberts limited his formulation to two free charge carriers and included a constant to account for the influence of bound electrons (19). He expressed the complex dielectric constant as

$$\bar{n}^2 = (n - ik)^2 = K_\infty - i \frac{\sigma_\infty}{\omega} - \frac{1}{\omega} \left(\frac{\sigma_1 \omega_1}{\omega - i\omega_1} + \frac{\sigma_2 \omega_2}{\omega - i\omega_2} \right) \quad (45)$$

where σ_1 and σ_2 are conductivities attributed to the two different charge carriers, ω_1 and ω_2 are the corresponding relaxation frequencies and K_∞ is the bound electron constant. Roberts used this expression to empirically correlate the optical properties of the noble and transition metals at room temperature.

In a later paper Roberts (20) generalized his formulation to include any number of free charge carriers and any number of bound electrons,

$$\bar{n}^2 = 1 + \sum_m \frac{K_{Om} \omega_{sm}^2}{\omega_{sm}^2 - \omega^2 + i\delta_m \omega_{sm} \omega} - \frac{1}{\omega} \sum_n \frac{\sigma_n \omega_{rn}}{\omega - i\omega_{rn}} \quad (46)$$

where ω_{sm} , ω_{rn} , δ_m , σ_n and K_{Om} are arbitrary coefficients which can be independently adjusted to characterize a particular metal. The first summation represents the contribution of m bound electrons and the second summation accounts for n types of free carriers. Roberts found

that three free carriers and two bound electron terms were sufficient to correlate the optical data of nickel at temperatures from 88°K to 473°K. Tungsten, from 298°K to 2400°K, required two free terms and three bound terms. Roberts (21) subsequently used the same expression with three free terms and a single bound term to correlate the optical data of copper.

The Drude-Roberts multi-electron theory has been successfully used to fit curves to normal monochromatic emittance data for a wide variety of metals. Edwards and deVolo (22) applied the two-electron theory to correlate room temperature emittance for 22 metals and high-temperature values for nickel and platinum. Seban (23) used the same two-electron theory for the transition metals at room temperature and 2000°R employing the values of the arbitrary parameters deduced by Roberts. Noland (24) found that many of the parameters exhibit a simple logarithmic dependence on temperature and extended the multi-electron theory to include this observation. He also evaluated total normal emissivity for several metals by integrating the expression derived from the Drude-Roberts theory.

Although the multi-electron theory is a useful tool in fitting curves to emittance data, it provides no insight into the physical mechanism of absorptivity or emissivity. A complicated algebraic expression is obtained when Eq. (46) is separated into its real and imaginary parts and the results used in Eq. (24). The many arbitrary coefficients which appear in the relations are purely empirical and can be determined only

by curve-fitting. As yet no theoretical interpretation of these coefficients has been proposed. In the case of a metal which requires, for example, three free terms and three bound terms, it is necessary to evaluate 15 arbitrary coefficients. Even if one or two of the coefficients could be related to atomic parameters, the influence of the parameters would be lost in the complexity of the expressions.

Electrical Resistivity

It is apparent from the preceding discussion that the optical properties of metals, and hence the thermal radiation properties, are closely related to the electrical conductivity or, alternately, the electrical resistivity. If the free-electron model is a reasonable approximation for metals, then the resistivity can be regarded as a measure of the electron damping. Metals exhibit resistivities of 1.5 to 150 microhm · centimeters at room temperature. Insulators, on the other hand, have resistivities which are ten to twenty orders of magnitude larger. To a first approximation, the resistivity of most metals varies linearly with temperature at high temperatures but decreases more rapidly at low temperatures.

It has been observed that experimental values of resistivity tend to approach a constant residual value as temperature approaches absolute zero. The resistivity can thus be regarded as consisting of a temperature-dependent ideal resistivity $\rho_i(T)$ and a temperature-independent residual resistivity ρ_0 ,

$$\rho = \rho_0 + \rho_i(T) , \quad \omega = 0 \quad (47)$$

This was first observed in 1860 by Matthiessen (25) who found that the change in resistance caused by a small concentration of an impurity metal in a solid solution was independent of temperature. The residual resistivity is now attributed to the effects of impurities and Eq. (47) is known as Matthiessen's rule. The important item to note here is that the residual resistivity is independent of temperature which implies that, at least in the far infrared, any impurity contribution to the electron damping coefficient would also be temperature-independent. For most metals the residual dc resistivity is a small fraction of the total resistivity at room temperature (see Appendix I).

The electrical resistivity is also related to the thermal conductivity as would be expected from the fact that metals are good conductors of heat as well as electricity. At a given temperature the thermal conductivity κ and the electrical conductivity σ are related by the Wiedemann-Franz law (26)

$$\frac{\kappa}{\sigma} = \text{constant} \quad (48)$$

In 1881, Lorenz (27) found that

$$\frac{\kappa}{\sigma T} = L \quad (49)$$

where L is a constant now known as the Lorenz number. Sadykov (28) has incorporated Eq. (49) into the Hagen-Rubens formula to obtain expressions for emissivity as a function of thermal conductivity.

Emissivity Calculations from Classical Theory

The use of classical theory to correlate and predict the normal monochromatic emissivity is illustrated in Figures 4, 5, 6, and 7 for copper, silver, gold and aluminum. The solid line represents the Hagen-Rubens formula, Eq. (44), using the dc conductivity values given in Appendix I. The Drude-Roberts two electron theory, as correlated by Edwards and deVolo (22), is also presented. The data are the values of Edwards and deVolo (22) and the data curves of Gubareff, Jansen and Torborg (29). The Hagen-Rubens formula predicts emissivity values which are low in the visible and near infrared; however, the correlation improves at longer wavelengths. It is interesting to note that, for the cases of copper and gold, the experimental data also lie above the Hagen-Rubens line for wavelengths greater than ten microns. This might cause one to question the generally accepted statement that Eq. (44) is valid for wavelengths greater than about six microns (1).

The two-electron theory, of course, exhibits good agreement with the data for wavelengths greater than about one micron. This is merely

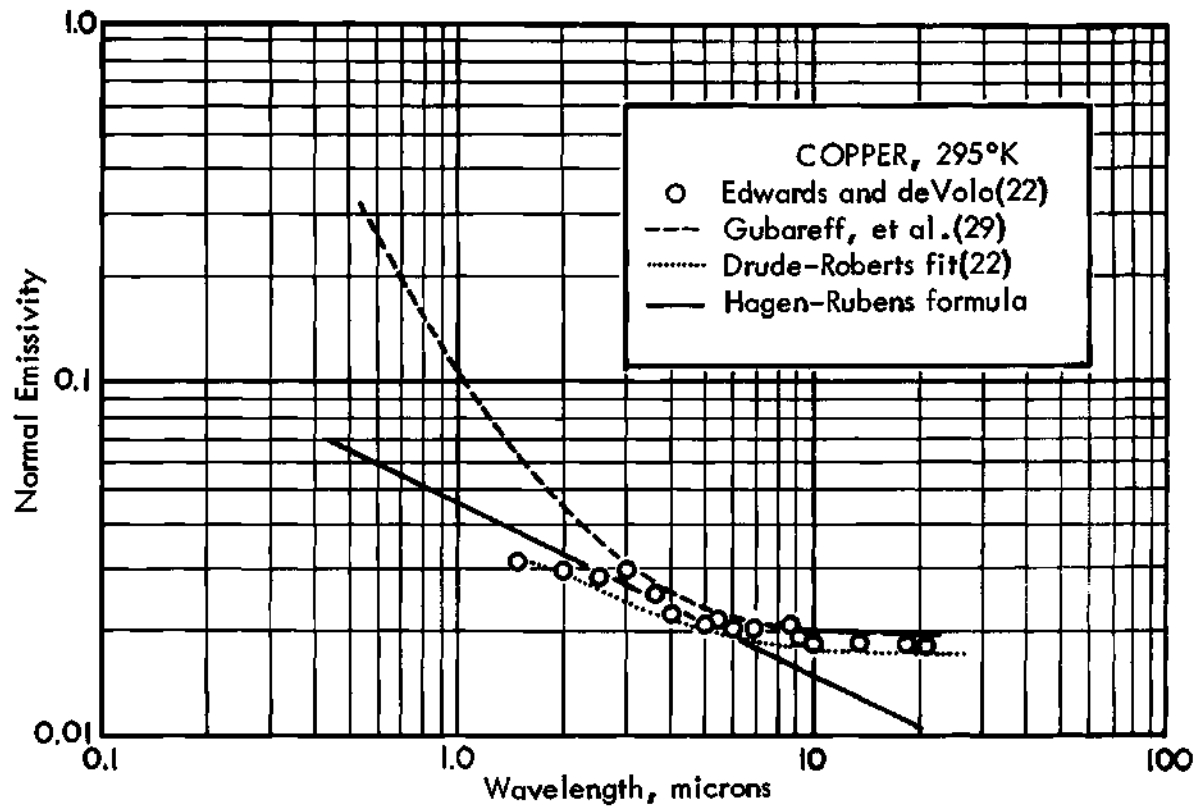


Figure 4. Monochromatic Emissivity of Copper at Room Temperature

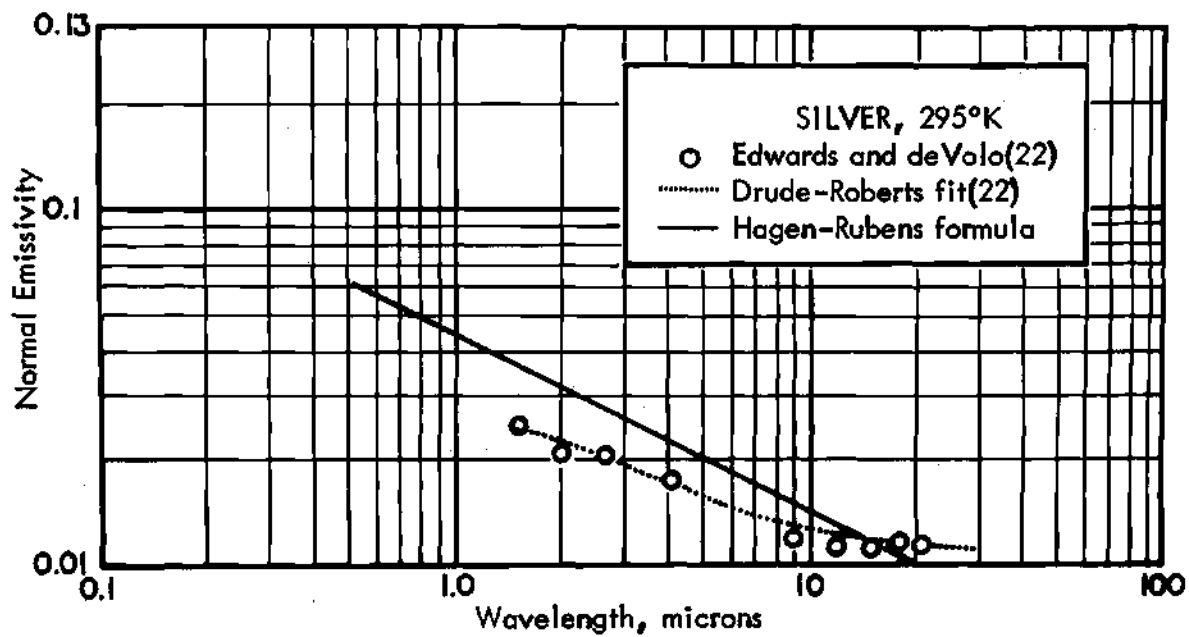


Figure 5. Monochromatic Emissivity of Silver at Room Temperature

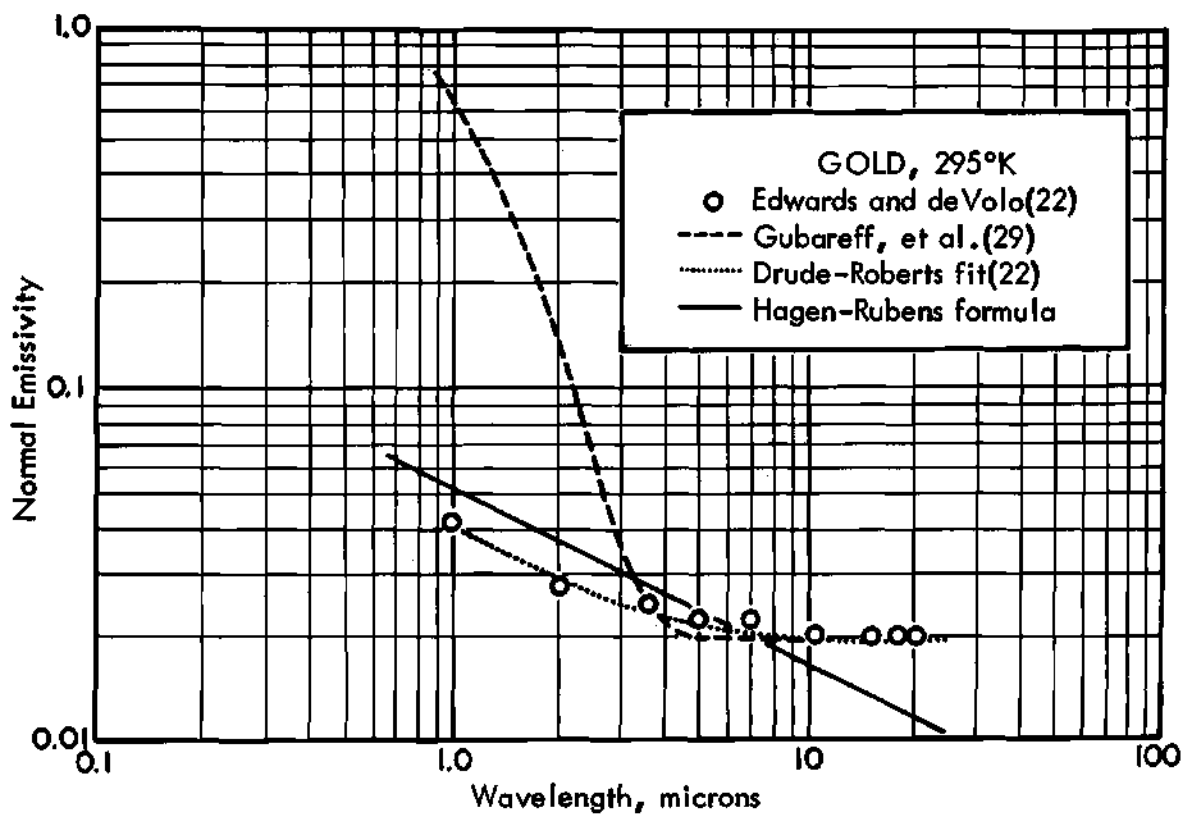


Figure 6. Monochromatic Emissivity of Gold at Room Temperature

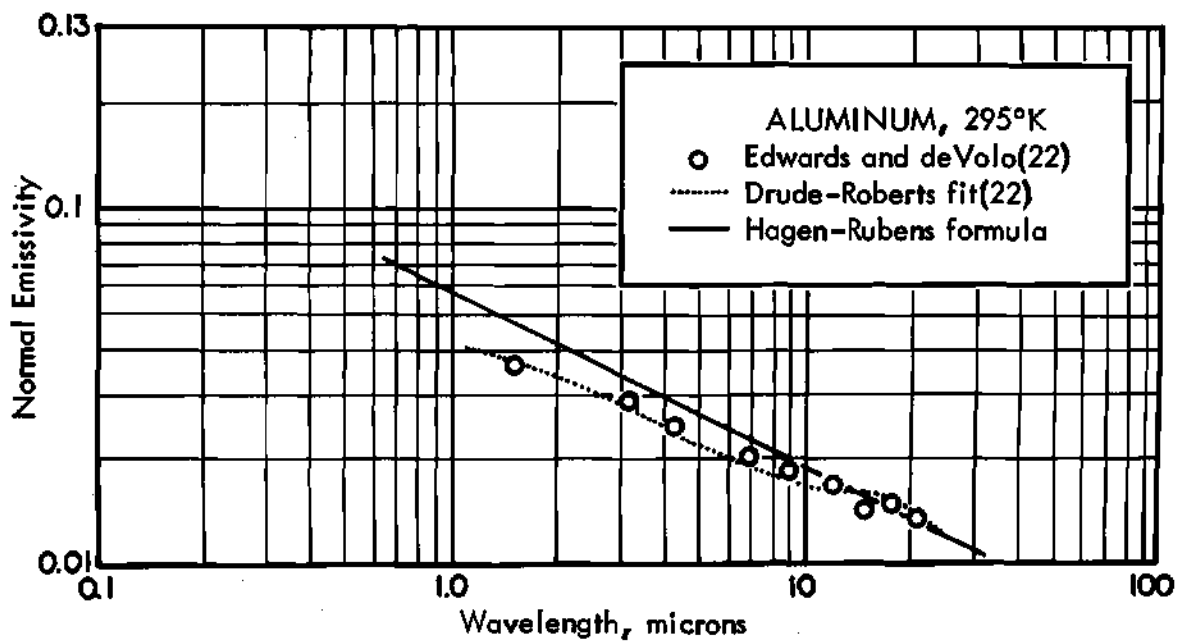


Figure 7. Monochromatic Emissivity of Aluminum at Room Temperature

a result of the fact that the arbitrary coefficients in the theory were selected to correlate the data of Edwards and deVolo. It is worthwhile to note that if these coefficients are selected to correlate the real and imaginary parts of the dielectric constant, they do not necessarily yield a good emissivity correlation. This is a result of the magnification of computational inaccuracies which occur when n and k are computed from $n^2 - k^2$ and $2nk$ and then ϵ is computed from the optical properties. For example, if the coefficients used by Roberts (16) to correlate the real and imaginary parts of \tilde{n}^2 are used to predict the normal monochromatic emissivity, poor agreement with experimental data is obtained. The two-electron theory is, therefore, essentially a means of fitting empirical curves to existing emissivity data. This fact, combined with the inaccuracies of the Hagen-Rubens formula, demonstrates the need for an improved theory of the thermal radiation properties.

CHAPTER III
A QUANTUM INTERPRETATION OF THE
THERMAL RADIATION PROPERTIES OF METALS

It has been noted that the classical theory of the optical properties of metals is developed from the solution of the equations of motion of the valence electrons subject to an electromagnetic field described by Maxwell's equations. Such an analysis yields the classical dispersion relations. These relations do not indicate temperature dependence and do not adequately specify the frequency dependence in the high-frequency portion of the spectrum. Such effects cannot be explained without the aid of a quantum model. Although considerable progress has been made in the use of quantum mechanics to explain, both qualitatively and quantitatively, the dc electrical properties of metals, the quantum dispersion theories are, as yet, incomplete. However, the optical properties of metals are closely related to their electrical properties. It is reasonable to expect, therefore, that quantum descriptions of the properties of a metal under the influence of a static electric field would provide a valuable tool in the study of dispersion phenomena. Furthermore, certain aspects of the well-developed quantum theory of semiconductors should be applicable because metals and semiconductors exhibit many properties which differ only in degree.

The theory developed in this chapter represents an extension of the quantum theory of electronic conduction in solids to include dispersion effects. We are concerned with a theoretical description of the phenomena which arise when an electromagnetic field interacts with matter. The conduction electrons play the central role in the transport of energy within a metal and the exchange of energy between a metal and an incident field. We must therefore deal with several topics which are familiar to the solid state physicist such as electron mobility, metallic band structure, electron-lattice interactions, electron-electron interactions, electron-impurity interactions and quantum wave propagation in periodic structures. It is unfortunate that recent theoretical developments in these and related areas of solid state physics have been so sparingly applied in the engineering study of the thermophysical properties of solids. However, the engineer who turns to the literature of the quantum theory of solids is usually frustrated if he seeks basic theory concerning the thermal radiation properties. He recognizes the important dependence of monochromatic properties on frequency but he finds that conductivity theory omits dispersion effects and that the more complex quantum theories of optical properties are incomplete.

The present theory represents a first step toward overcoming these deficiencies from an engineering viewpoint. It is developed within the framework of the quantum theory of solids but in such a manner that the theory retains at least a qualitative usefulness in engineering analysis.

The solid state physicist usually develops a theory in very general terms based on a detailed atomic model and then attempts to apply it to a restricted case. He is usually not interested in such macroscopic parameters as the thermal radiation properties. Instead, he is concerned with atomic detail and if his theory incorporates too many simplifying assumptions, these details are lost. His theory, therefore, usually leads to expressions which can be applied to only a limited number of cases. For example, the modern quantum theory of vibronic emission and absorption in solids, which is closely related to the theory of thermal radiation properties, is ordinarily presented as a set of equations which yield the Hamiltonian matrix elements which describe the electron transitions (30). These equations, however, are expressed in terms of quantum operators which can be determined only if a relatively simple atomic model is assumed or if the analysis is restricted to a specific solid or group of similar solids. The present approach is somewhat different. Rather than retain the complex details of a sophisticated model throughout the analysis, we shall incorporate several simplifications at the beginning and attempt to interpret the results within the framework of these assumptions. The fact that we are ultimately interested in macroscopic properties tends to allow a simplification of the atomic model and this, in turn, enables us to extend the theory.

The Model of the Atomic System

In order to obtain a theoretical understanding of absorption in the visible and infrared portions of the spectrum, it is necessary to develop analytical expressions for the rate at which energy is expended by the electromagnetic field as it influences the atomic processes in a metal. The first requirement, therefore, is an atomic model of the metal which defines the mechanisms by which the conduction electrons can gain or lose energy. We shall assume that the mechanisms by which a metal can absorb energy from an electromagnetic field in the frequency range of interest in thermal radiation are as follows:

1. Energy is absorbed in the acceleration of free electrons.
2. Electron motion is damped by interaction with the crystal lattice.
3. Electron motion is influenced by the mutual interaction of free electrons.
4. Electron motion is damped by interactions with impurities in the crystal lattice.
5. Energy can be absorbed by the bound electrons.

The classical free-electron theory accounts for the fact that the external field provides energy to accelerate the conduction electrons. It also includes a simplified model of electron damping, as described in Chapter II, but does not account for the details of the damping mechanism. The positively-charged ions which constitute the lattice array contribute

an internal potential field to which the conduction electrons are subjected. It is reasonable to assume that the motion of the electrons is influenced by this potential and that an electron can thereby exchange energy with the ions. Because each electron is negatively charged, they exhibit a mutual repulsion which can also affect their individual motion. The presence of impurities at lattice sites provides an additional damping mechanism because the interaction between an electron and an impurity ion is usually different in nature from the interaction between the electron and an ion of the metal. Finally, an electromagnetic field of sufficient strength might influence the local motion of the outer bound electrons of the ion. This provides another mechanism by which a metal can absorb energy from the field.

The theoretical task is that of developing analytical expressions which account for as many of these interactions as possible and which relate the thermal radiation properties of a metal to its temperature and the frequency of the incident electromagnetic field. This requires a solution of the equation of motion of an electron which is subject to the interactions. From the quantum viewpoint, this equation of motion is Schroedinger's equation rather than the Newtonian relation used in classical theory (31). Each mechanism by which the electron energy is changed contributes a term to the Schroedinger equation. To obtain a solvable form of the Schroedinger equation it is usually necessary to make assumptions concerning the relative importance of the various mechanisms. We

shall begin by assuming that the dominant interactions are the acceleration of the electron by the incident field and the damping of its motion by interaction with the lattice ions. The following arguments can be made to justify this assumption in a first analysis.

Both the electron-lattice interaction and the electron-electron interaction can be studied in terms of the relaxation time and mean free path of the electron. Kittel (9) shows that, except at very low temperatures, the mean free path for electron-electron collisions in a free electron gas is at least ten times longer than the mean free path for electron-lattice interactions. This means that, on the average, an electron will undergo ten interactions with lattice ions for each interaction with another electron. This observation also results from a study of the various terms which contribute to the thermal conductivity of metals (32). Because electrons play an important role in the transport of heat through a solid, the high thermal conductivities of metals indicate that electron-electron interactions do not significantly inhibit heat transfer. Such observations support the assumption that electron-lattice interactions have a much more significant influence on the motion of electrons in metals than do electron-electron interactions.

Matthiessen's rule, discussed in Chapter II, indicates that the effect of impurities on electron mobility in metals is not a function of temperature. Furthermore, because the residual resistivity which represents the influence of impurities is very small compared with the resistivity

at room remperature for commercially pure metals, it follows that the electron damping is predominantly due to mechanisms other than electron-impurity interactions except perhaps at very low temperatures. We shall therefore assume that the effects of impurities are small compared with the electron-lattice interaction.

The arguments given above lend strong support to the assumption that the electron-lattice interaction is the principal damping mechanism. This assumption is made even more valid by the fact that we are concerned with the temperature-dependence of the thermal radiation properties above room temperature. Nonetheless, although neither will be included in the initial stages of the analytical development, we shall later consider the qualitative influence of both the electron-electron and the electron-impurity interactions.

The influence of bound electrons becomes important near field frequencies which excite resonant vibrations. The resulting bound resonance terms enter directly into the classical dispersion relations for insulators (7). No such resonant frequencies appear in the classical free-electron theory of metals. Experimental measurements of the optical properties of metals, however, reveal irregularities at various frequencies in the ultraviolet. These are generally attributed to the absorption of energy by surface and volume plasmons as well as core electrons bound to the metal ions and appear only when the energy density of the field is sufficient to excite such electrons (33). The analysis of resonance

absorption involves a sophisticated application of quantum theory usually limited to a specific class of metals. Because this type of absorption depends on the degree to which the outer ion electrons are bound to the core, it varies with the position of a metal in the periodic table of elements. The fact that resonance occurs at relatively high frequencies reduces its importance in a study of thermal radiation properties. Accordingly, we shall assume that resonance absorption, like the influence of the electron-electron interaction, is small compared to the effects of the electron-lattice interaction. This assumption carries with it some implications which enter into the quantum analysis and, in effect, defines the high frequency limit to which the theory applies. We shall find, however, that some account must be taken of this absorption mechanism if we wish to apply the theory to the transition metals.

The theory which follows makes repeated use of the definitions and concepts of elementary quantum mechanics and the quantum theory of solids. Because this thesis represents a dissertation in the engineering sciences, not all readers will be familiar with the necessary background material. Some of the pertinent concepts of elementary quantum theory are outlined in Appendix II. For additional background information, the reader is urged to consult the standard literature in these areas. Most of the fundamental concepts are treated by Schiff (31) and Slater (34). The elementary theory of solids is presented by Seitz (35) and Kittel (9) and applied to metals by Wilson (36). The text by Mott and Jones (37) continues

to be important in the field. The more advanced quantum theory of solids is treated by Kittel (38) and Ziman (39). An excellent elementary account of electronic conduction in solids is given by Blatt (40).

The Quantum Interaction of Radiation and Matter

For the purpose of developing expressions for the thermal radiation properties of metals, we shall consider conditions defined as follows.

When an electromagnetic field is incident on a metal, energy is absorbed when a conduction electron absorbs a quantum of electromagnetic energy (a photon) and undergoes a transition from a state characterized by wave vector \vec{k} to one characterized by wave vector \vec{k}' . Energy is emitted when a conduction electron undergoes a transition to a lower energy state with the emission of a photon into the field. Simultaneously, the conduction electrons can exchange energy with the lattice by transitions which involve the absorption or emission of a quantum of lattice vibrational energy (a phonon). We define $P_r^s(\vec{k} \rightarrow \vec{k}')$ as the probability per unit time for a conduction electron to make a transition from state \vec{k} to a final state \vec{k}' with simultaneous photon and phonon emissions and absorptions when the state \vec{k} is completely filled and the state \vec{k}' is completely empty. The subscript "r" denotes the photon process and will be written "e" for photon emission and "a" for photon absorption. Similarly, the superscript "s" refers to the phonon process and will also be written "e" for emission and "a" for absorption. Because electrons obey

the Fermi-Dirac statistics, the probability that state \vec{k} with energy E_k is filled at temperature T is given by the Fermi function

$$g(E) = \frac{1}{e^{(E-E_f)/KT} + 1} \quad (50)$$

where E_f is the Fermi energy and K is the Boltzmann constant. Thus, the total probability that an electron will make a transition from an initial state \vec{k} to any other state which is empty by any of the four processes designated by the phonon and photon subscripts is

$$P_r^S(\vec{k}) = 2 \sum_{k'} [1 - g(E_{k'})] P_r^S(\vec{k} \rightarrow \vec{k}') \quad (51)$$

where the factor 2 accounts for the Pauli exclusion principle that two electrons of opposite spin can occupy a state with the same wave vector and energy.

The effects of these electron transitions are represented by the average of this probability over all of the initially-occupied states according to Fermi-Dirac statistics. This average is

$$\overline{P_r^S} = \frac{2}{\sum_k g(E_k)} \sum_k \sum_{k'} g(E_k) [1 - g(E_{k'})] P_r^S(\vec{k} \rightarrow \vec{k}') \quad (52)$$

The power expenditure of the electromagnetic field is the total power absorbed minus the power emitted into the external field, or

$$W(\omega, T) = \sum_s \hbar\omega (\bar{P}_a^s - \bar{P}_e^s) \quad (53)$$

Part of the temperature dependence of W is due to the Fermi-Dirac statistics of the electron distribution and part is due to the Bose-Einstein phonon distribution which enters into the Hamiltonian average over the phonon states.

If $\Psi_{\mathbf{k}}$ is the wave function representing the initial electron state with wave vector $\vec{\mathbf{k}}$ and $\Psi_{\mathbf{k}'}$ is the wave function representing the final electron state with wave vector $\vec{\mathbf{k}'}$, the probability per unit time that an electron will undergo a transition from state $\Psi_{\mathbf{k}}$ to state $\Psi_{\mathbf{k}'}$ can be written in Dirac notation as (30)

$$P(\vec{\mathbf{k}} \rightarrow \vec{\mathbf{k}'}) = \frac{2\pi}{\hbar^2} |M_{\mathbf{k}'}|^2 g(E_{\mathbf{k}'}) \quad (54)$$

where $g(E_{\mathbf{k}'})$ is the density of final states given by Eq. (50) and $M_{\mathbf{k}'}$ is defined as

$$M_{\mathbf{k}'} = \langle \Psi_{\mathbf{k}'} | H' | \Psi_{\mathbf{k}} \rangle \quad (55)$$

where H' is the Hamiltonian operator for the interactions between the electron and both the incident field and the lattice. In order to evaluate the Hamiltonian and the corresponding elements of the transition matrix, it is necessary to consider the Schrodinger equation.

The Schroedinger Equation and the Hamiltonian

In the development of the Hamiltonian function we shall treat the electromagnetic field classically, i.e. we shall assume that the field can be represented by a vector potential \vec{A} and a scalar potential ϕ . A complete treatment of the field in the framework of quantum electrodynamics is beyond the scope of this research; nonetheless, we shall retain the essential feature of quantization of the field in that we recognize that the field and the atomic system can exchange energy only in quanta of $h\nu$. The formulation of the Hamiltonian function follows the treatment by Sokolov (41).

Consider an electromagnetic field described by an electric field vector \vec{E} and a magnetic induction vector \vec{B} . The field can be expressed in terms of a vector potential \vec{A} and a scalar potential ϕ which are related to \vec{E} and \vec{B} by (8),

$$\vec{B} = \nabla \times \vec{A} \quad (56)$$

and

$$\vec{E} = -\nabla\phi - \frac{1}{c} \frac{\partial \vec{A}}{\partial t} \quad (57)$$

The equation of motion for an electron in an electromagnetic field is (34)

$$m \frac{\partial^2 \vec{r}}{\partial t^2} = e \left[\vec{E} + \left(\frac{\partial \vec{r}}{\partial t} \times \vec{B} \right) \right] \quad (58)$$

We can obtain a relation for the quantum-mechanical Hamiltonian operator by determining the classical Hamiltonian function for this equation of motion and by replacing the variables with their corresponding quantum operators. This can be done by demonstrating the equivalence of Eq. (58) with the Hamilton form of the equations of motion,

$$\frac{\partial x_i}{\partial t} = \frac{\partial \mathcal{H}}{\partial p_i} ; \quad \frac{\partial p_i}{\partial t} = - \frac{\partial \mathcal{H}}{\partial x_i} \quad (i = 1, 2, 3) \quad (59)$$

where p_i is the component of momentum in the x_i direction and \mathcal{H} is the classical Hamiltonian. Equations (58) and (59) are equivalent if the Hamiltonian is of the form,

$$\mathcal{H} = \frac{1}{2m} \left(\vec{p} - \frac{e}{c} \vec{A} \right)^2 + e\phi \quad (60)$$

Because the quantum operator corresponding to momentum is $\hat{p} = -i\hbar \nabla$, we can write the Hamiltonian for an electron in an electromagnetic field as

$$H = \frac{1}{2m} \left(-i\hbar \nabla - \frac{e}{c} \vec{A} \right)^2 + e\phi \quad (61)$$

In our particular problem, however, we have additional complexities. We must account for the periodic potential of the lattice ions and the deformation of this potential caused by thermal vibrations. These factors contribute some form of potential which is a function of the position of the electron. We can therefore express the quantum Hamiltonian operator as

$$H = \frac{1}{2m} \left(-i\hbar \nabla - \frac{e}{c} \vec{A} \right)^2 + e\phi + V(\vec{r}, t) \quad (62)$$

where the potential $V(\vec{r}, t)$ accounts for the interactions. The first term on the right side of Eq. (62) can be written

$$\left(\hat{p} - \frac{e}{c} \vec{A} \right)^2 = \left(\hat{p}_x - \frac{e}{c} A_x \right)^2 + \left(\hat{p}_y - \frac{e}{c} A_y \right)^2 + \left(\hat{p}_z - \frac{e}{c} A_z \right)^2$$

Each of these terms can be written in the following form:

$$\begin{aligned} \left(\hat{p}_x - \frac{e}{c} A_x \right)^2 &= \left(\hat{p}_x - \frac{e}{c} A_x \right) \left(\hat{p}_x - \frac{e}{c} A_x \right) = \hat{p}_x^2 - \frac{e}{c} A_x \hat{p}_x - \frac{e}{c} \hat{p}_x A_x + \frac{e^2}{c^2} A_x^2 \\ &= \hat{p}_x^2 - \frac{2e}{c} \hat{p}_x A_x + \frac{e^2}{c^2} A_x^2 + \frac{e}{c} (\hat{p}_x A_x - A_x \hat{p}_x) \end{aligned}$$

We can now employ the following commutation relation for the momentum operator (38)

$$[\hat{p}_x, A_x] \equiv (\hat{p}_x A_x - A_x \hat{p}_x) = -i\hbar \frac{\partial A_x}{\partial x} \quad (63)$$

Then

$$(\hat{p}_x - \frac{e}{c} A_x)^2 = \hat{p}_x^2 - \frac{2e}{c} \hat{p}_x A_x - \frac{i e \hbar}{c} \frac{\partial A_x}{\partial x} + \frac{e^2}{c^2} A_x^2$$

Similar relations hold for the other coordinate directions; therefore

$$(\hat{p} - \frac{e}{c} \vec{A})^2 = \hat{p}^2 - \frac{2e}{c} \hat{p} \vec{A} - \frac{i e \hbar}{c} \nabla \cdot \vec{A} + \frac{e^2}{c^2} A^2 \quad (64)$$

If the Coulomb gauge transformation is used, it is always possible to select the vector potential so that $\nabla \cdot \vec{A} = 0$ and $\Phi = 0$ (42).

Furthermore, for fields of the magnitude encountered in thermal radiation the term in A^2 is negligible compared with the term in \vec{A} (43). The term in A^2 is related to processes in which two photons simultaneously participate. Such processes do not enter into emission and absorption phenomena but are important in treating the interaction of matter with static magnetic fields.

If these simplifications are introduced into Eq. (62), the Hamiltonian operator can be written,

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{i\hbar e}{mc} \nabla \cdot \vec{A} + V(\vec{r}, t) \quad (65)$$

From the vector relation $\nabla \cdot (\vec{A}\Psi) = \vec{A} \cdot \nabla\Psi + \Psi(\nabla \cdot \vec{A}) = \vec{A} \cdot \nabla\Psi$, we can write,

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{i\hbar e}{mc} \vec{A} \cdot \nabla + V(\vec{r}, t) \quad (66)$$

Thus the Schrodinger equation for an electron subjected to a perturbing external electromagnetic field and a perturbing interaction potential $V(\vec{r}, t)$ is

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi = -\frac{\hbar^2}{2m} \nabla^2 \Psi + \left\{ \frac{i\hbar e}{mc} \vec{A} \cdot \nabla + V(\vec{r}, t) \right\} \quad (67)$$

The Electron-Lattice Interaction

A time-dependent perturbation solution of the Schrodinger equation provides the transition probabilities necessary to compute the dispersion properties of a solid. In order to carry out such a solution of Eq. (67) we must have available some mathematical form for the interaction potential. Our model of the atomic system includes interactions between the conduction electrons and the ions which constitute the lattice array. Hence, the interaction potential $V(\vec{r}, t)$ represents the potential which gives rise to the electron-phonon interaction.

Consider an electron moving among the ions of a crystal lattice in the absence of an external electromagnetic field. The potential to which the electron is subjected can be treated as consisting of two parts. First, there is an ideal periodic potential field due to the charges of the ions if the ions remained stationary in the lattice. The spatial periodicity of this potential $V_i(\vec{r})$ is related to the ion spacing and the potential is a function only of the position of the electron. The ions, however, do not remain stationary. They are thermally excited and vibrate about some equilibrium position. This vibration causes a time-dependent distortion of the crystal potential field which can be regarded as the source of the second part of the total potential. Hence, we can write

$$V = V(\vec{r}, t) = V_d(\vec{r}, t) + V_i(\vec{r}) \quad (68)$$

where $V_i(\vec{r})$ represents the potential field in an array of ideal stationary ions and $V_d(\vec{r}, t)$ represents the change of potential caused by thermal vibrations.

It has been found that when a particle moves in a perfect periodic potential, such as that represented by $V_i(\vec{r})$, and is acted upon by an external force F , it does not exhibit an acceleration F/m but rather F/m^* , where m^* is termed the effective mass of the particle (44). The effective mass accounts for the interaction between the particle and the

ideal periodic lattice potential $V_i(\vec{r})$. It can be greater or less than the rest mass of the particle and, for an isotropic lattice, is given by

$$m^* = \frac{\hbar^2}{d^2E/dk^2} \quad (69)$$

From the concepts of band theory (9) it can be seen that m^* is negative for states near the top of a band, positive for states near the bottom and infinite for some energy level within the band. By imposing certain limitations on the type of transitions which can occur, an analysis can be conducted with constant values of the effective mass. Thus the effects of the periodic lattice potential can be included in the analysis by using the effective mass rather than the rest mass of the electron.

It follows from Eq. (69) that the effective mass is constant if the energy is a quadratic function of the wave vector. Such a relationship holds in the case of a spherical Fermi surface. The concept of the Fermi surface arises in the study of the properties of a free-electron gas. At absolute zero temperature the electrons occupy states in wave vector space whose outer boundaries form a surface of constant energy which is termed the Fermi surface. For free electrons, this energy surface is spherical. The atomic model postulated earlier in this chapter is one of nearly free electrons, i.e. the conduction electrons are assumed to move

approximately freely between interactions with the lattice. For a model of this type, the Fermi surface is nearly spherical except in regions near the boundaries of the Brillouin zones and the electron energy is given by (36)

$$E_k = \frac{\hbar^2 k^2}{2m^*} \quad (70)$$

The assumption of a spherical Fermi surface is made in nearly every analysis of the electrical transport properties of metals. This is a result of two factors. First, a theory which attempts to account for the intricate topological details of the Fermi surface would be extremely complex and would certainly be beyond the scope of a study designed to gain insight into the nature of the thermal radiation properties of metals. Secondly, very little is known about the shape of the Fermi surface of most metals. Sodium and aluminum are examples where detailed work has been done to define the topology of the Fermi surface. A discussion of Fermi surface topology is presented by Ziman (39).

It is also difficult to evaluate the inaccuracy introduced by the assumption of spherical Fermi surfaces. Although some qualitative statements can be offered, it is usually necessary to evaluate the errors based on the ultimate results of the theory. For example, part of the error in theoretical values of electrical conductivity can be attributed

to the assumption of a spherical Fermi surface. It has been found that the spherical assumption introduces very little error in values of the dc conductivity of most of the face-centered, body-centered and hexagonal cubic lattices (36). Schocken (45) finds that the spherical approximation is even adequate for a polycrystalline sample of a metal which exhibits energy anisotropy in single crystal form. Of course, considerable error is involved in the use of such an approximation for the transition metals because of their overlapping band structure. This will be discussed when we qualitatively treat the transition metals in a later section.

Thus, we shall assume a spherical Fermi surface in our analysis. This enables us to use the concept of an isotropic effective mass to account for the periodic lattice potential. We shall also assume isotropic lattice characteristics on the atomic scale. This assumption, which is valid for the cubic lattice structures, allows us to treat the effective mass as a scalar rather than a tensor. If we replace the rest mass in Eq. (67) by the effective mass of the electron, the Schroedinger equation becomes

$$i\hbar \frac{\partial \Psi}{\partial t} = - \frac{\hbar^2}{2m^*} \nabla^2 \Psi + \left\{ \frac{i\hbar e}{m^* c} \vec{A} \cdot \nabla + V_d(\vec{r}, t) \right\} \Psi \quad (71)$$

The time-dependent deformation potential $V_d(\vec{r}, t)$, which represents the distortion of the periodic lattice potential caused by thermal

vibrations, is the field which gives rise to the electron-phonon interaction. Bardeen and Shockley (46) have shown that the deformation potential can be expressed as

$$V_d(\vec{r}, t) = E_d \Delta \quad (72)$$

where E_d is a constant with units of energy and $\Delta = \delta V/V$ is the lattice dilation caused by thermal vibration. For an isotropic lattice, the dilation can be written as (38),

$$\Delta(\vec{r}, t) = i \sum_{\vec{q}} \left(\frac{\hbar}{2\rho_p \omega_{\vec{q}}} \right)^{1/2} (a_{\vec{q}} e^{i\vec{q} \cdot \vec{r}} - a_{\vec{q}}^+ e^{-i\vec{q} \cdot \vec{r}}) \left| \vec{q} \right| \quad (73)$$

where ρ_p is the phonon density, \vec{q} is the phonon wave vector, $\omega_{\vec{q}}$ is the phonon angular frequency given by the quantum condition $E_{\vec{q}} = \hbar \omega_{\vec{q}}$ and $a_{\vec{q}}^+$ and $a_{\vec{q}}$ are the phonon creation and annihilation operators respectively. These boson operators are such that, if $n_{\vec{q}}$ is the number of phonons in state \vec{q} , then (40)

$$\langle n_{\vec{q}} - 1 \mid a_{\vec{q}} \mid n_{\vec{q}} \rangle = \sqrt{n_{\vec{q}}} \quad (74)$$

$$\langle n_{\vec{q}} + 1 \mid a_{\vec{q}}^+ \mid n_{\vec{q}} \rangle = \sqrt{n_{\vec{q}} + 1} \quad (75)$$

By including the time-dependence $e^{-i\omega_{\vec{q}}t}$ of the phonon state vector, it follows that the phonon operators can be written

$$a_{\vec{q}} = \sqrt{n_{\vec{q}}} e^{-i\omega_{\vec{q}}t} \quad (76)$$

$$a_{\vec{q}}^{\dagger} = \sqrt{n_{\vec{q}} + 1} e^{-i\omega_{\vec{q}}t} \quad (77)$$

where the number of phonons in state \vec{q} is given the Bose-Einstein distribution function

$$n_{\vec{q}} = \frac{1}{e^{E_{\vec{q}}/KT} - 1} \quad (78)$$

If Eqs. (76) and (77) are used in Eq. (73), the deformation potential can be expressed as

$$V_d(\vec{r}, t) = iE_d \sum_{\vec{q}} \left(\frac{\hbar}{2\rho_p \omega_{\vec{q}}} \right)^{1/2} \frac{1}{q} \left[\sqrt{n_{\vec{q}}} e^{i(\vec{q} \cdot \vec{r} - \omega_{\vec{q}}t)} - \sqrt{n_{\vec{q}} + 1} e^{i(\vec{q} \cdot \vec{r} - \omega_{\vec{q}}t)} \right] \quad (79)$$

where $q = |\vec{q}|$.

With this relation for the deformation potential we can use standard time-dependent perturbation theory to obtain an approximate solution of the Schroedinger equation. There are several assumptions implicit in the form given by Eq. (79) for the deformation potential. First, it included the effect of longitudinal acoustic phonons only; it does not

account for transverse waves. This assumption can be justified for our problem by noting, from a more general analysis (38), that the effects of transverse waves are included in terms which contain the very small scalar product of the phonon wave vector and the unit vector in the transverse direction.

A second assumption implicit in Eq. (79) is that the analysis is limited to the normal or N processes for which the wave vectors of the electron, \vec{k} and \vec{k}' , are related to that of the phonon by momentum conservation in the form

$$\vec{k} - \vec{k}' \pm \vec{q} = 0 \quad (80)$$

The second possibility is the Umklapp or U process for which

$$\vec{k} - \vec{k}' \pm \vec{q} = \vec{G} \quad (81)$$

where \vec{G} is a wave vector in the reciprocal lattice. This process influences the electron-electron interaction and is discussed in Appendix III.

Electron Transition Probabilities

The Schroedinger equation given by Eq. (71) can be written

$$(H^0 + H') \Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (82)$$

where H^0 is the unperturbed (zero-order) Hamiltonian,

$$H^0 = - \frac{\hbar^2}{2m^*} \nabla^2 \quad (83)$$

and H' is the perturbation term,

$$H' = \frac{i\hbar e}{m^* c} \mathbf{A} \cdot \nabla + V_d(\vec{r}, t) \quad (84)$$

The stationary states of the conduction electrons are given by the solution of the unperturbed wave equation,

$$H^0 \Psi^0 = i\hbar \frac{\partial \Psi^0}{\partial t} \quad (85)$$

These states are represented by the wave functions

$$\psi_{\mathbf{k}}^0 = e^{i(\vec{k} \cdot \vec{r} - E_{\mathbf{k}} t / \hbar)} \quad (86)$$

The energy of the stationary states is a function of $\mathbf{k} = |\vec{k}|$ only and is given by Eq. (70).

The total Hamiltonian, $H^0 + H'$, includes the influence of the external electromagnetic field and the thermal vibrations of the lattice. These effects are treated as perturbations of the electron motion and are separated into the perturbation Hamiltonian H' . We then utilize the familiar methods of time-dependent perturbation theory to determine the electron transition probabilities.

It is convenient to express the perturbation Hamiltonian as the sum of two terms, one of which gives rise to the electron-photon interaction H_1' , and one which represents the electron-phonon interactions H_2' . The vector potential of the field can be expressed in terms of the electric field vector \vec{E}_0 and the photon wave vector \vec{p} (41)

$$\vec{A} = \frac{c\vec{E}_0}{2i\omega} \left[e^{i(\vec{p} \cdot \vec{r} - \omega t)} - e^{-i(\vec{p} \cdot \vec{r} - \omega t)} \right] \quad (87)$$

Then

$$H_1' = \frac{\hbar e\vec{E}_0}{2m^*\omega} \left[e^{i(\vec{p} \cdot \vec{r} - \omega t)} - e^{-i(\vec{p} \cdot \vec{r} - \omega t)} \right] \quad (88)$$

and from Eq. (79)

$$H_2' = iE_d \sum_q \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \left[\sqrt{n_q} e^{i(\vec{q} \cdot \vec{r} - \omega t)} - \sqrt{n_q + 1} e^{-i(\vec{q} \cdot \vec{r} - \omega t)} \right] \quad (89)$$

If these relations are used in a time-dependent perturbation analysis (see Appendix II), the time rate-of-change of the wave function expansion coefficients is

$$i\hbar \sum_{\mathbf{k}} \frac{\partial a_{\mathbf{k}}(t)}{\partial t} \psi_{\mathbf{k}}^0 = \sum_{\mathbf{k}} a_{\mathbf{k}}(t) \left\{ \frac{i\hbar e(\vec{E}_0 \cdot \vec{k})}{2m^* \omega} \left[e^{i(\vec{p} \cdot \vec{r} - \omega t)} e^{-i(\vec{p} \cdot \vec{r} - \omega t)} \right] \right. \quad (90)$$

$$+ iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} \left[\sqrt{n_q} e^{i(\vec{q} \cdot \vec{r} - \omega_q t)} \right.$$

$$\left. \left. - \sqrt{n_q + 1} e^{-i(\vec{q} \cdot \vec{r} - \omega_q t)} \right] \right\} \psi_{\mathbf{k}}^0$$

The electron can undergo four possible transitions:

1. It can absorb a photon of wave vector \vec{p} from the radiation field and go from state \vec{k} to state $\vec{k} + \vec{p}$.
2. It can emit a photon into the field and go from state \vec{k} to state $\vec{k} - \vec{p}$.
3. It can absorb a phonon of wave vector \vec{q} and go from state \vec{k} to state $\vec{k} + \vec{q}$.
4. It can emit a phonon and go from state \vec{k} to state $\vec{k} - \vec{q}$.

The Hamiltonian contains a term corresponding to each of these processes. The first term on the right in Eq. (90) involves a photon absorption, the second a photon emission, the third a phonon absorption and the fourth a phonon emission. If we proceed with the perturbation analysis, following

the steps outlined in Appendix II, we obtain a first-order coefficient given by (see Appendix IV)

$$\begin{aligned}
 a_{\mathbf{k}'}^{(1)} = & \frac{\hbar e(\vec{E}_0 \cdot \vec{k})}{2im^* \omega} \left[\delta_{\mathbf{k}', \mathbf{k}+\mathbf{p}} \left(\frac{e^{i(\omega_{\mathbf{k}+\mathbf{p}, \mathbf{k}-\omega)t-1}}}{\hbar(\omega_{\mathbf{k}+\mathbf{p}, \mathbf{k}-\omega})} \right) \right. \\
 & - \delta_{\mathbf{k}', \mathbf{k}-\mathbf{p}} \left(\frac{e^{i(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega)t-1}}}{\hbar(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})} \right) \left. \right] \\
 & - iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} \left[\delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}} \sqrt{n_{\mathbf{q}}} \left(\frac{e^{i(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega)t-1}}}{\hbar(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})} \right) \right. \\
 & \left. - \delta_{\mathbf{k}', \mathbf{k}-\mathbf{q}} \sqrt{n_{\mathbf{q}}+1} \left(\frac{e^{i(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega)t-1}}}{\hbar(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}+\omega_{\mathbf{q}}})} \right) \right]
 \end{aligned} \tag{91}$$

where δ_{mn} is the Kroenecker delta and

$$\omega_{\mathbf{k}, \mathbf{m}} = (E_{\mathbf{k}} - E_{\mathbf{m}})/\hbar \tag{92}$$

Because of the presence of the Kroenecker delta terms in Eq. (91), the first-order coefficient and the corresponding transition probability is non-zero only if the initial and final electron wave vectors are the same, that is, if $\vec{k} = \vec{k} \pm \vec{p}$ or $\vec{k} = \vec{k} \pm \vec{q}$. But we have assumed a spherical Fermi surface; hence the initial and final energies are the

same if the initial and final electron states are characterized by the same wave vector. Energy conservation in the case of absorption of a photon by a free electron, for example, would require that $E_k - E_{k'} + \hbar\omega = 0$. But if $E_k = E_{k'}$, energy would not be conserved because $\hbar\omega$ is never zero. Hence, interactions between a free electron and either a photon or a phonon, within the framework of the specific model which we have adopted, must yield only virtual transitions, that is, transitions in which energy is not conserved (47). It follows that, according to our model, visible and infrared absorption is a result of processes in which a photon is absorbed and a phonon emitted. This also includes the acceptable process of absorption or emission of both a photon and a phonon. Similarly, emission involves the simultaneous absorption of a phonon and emission of a photon. Such processes do not appear in the first-order coefficients. They are represented by the terms in the second-order coefficients which are bilinear in the photon and phonon matrix elements.

The second-order terms are obtained by substituting Eq. (91) into the relation for the time rate-of-change of the coefficients, collecting terms bilinear in the photon and phonon Hamiltonians and integrating over time from 0 to t . The result is

$$\begin{aligned}
a_{\vec{k}\pm\vec{p}\pm\vec{q}}^{(2)} = & \pm \frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \left\{ \frac{\sqrt{n_q}}{\sqrt{n_q + 1}} \right\} \vec{E}_0 \cdot \left[\left(\frac{\vec{k}\pm\vec{q}}{\hbar(\omega_{\vec{k}\pm\vec{q}}, \vec{k}\mp\omega_q)} \right) \right. \\
& + \left. \frac{\vec{k}}{\hbar(\omega_{\vec{k}\pm\vec{p}}, \vec{k}\mp\omega)} \right) \frac{e^{iW_1 t/\hbar-1}}{W_1} - \frac{\vec{k}\pm\vec{q}}{\hbar(\omega_{\vec{k}\pm\vec{q}}, \vec{k}\mp\omega_q)} \left(\frac{e^{iW_2 t/\hbar-1}}{W_2} \right) \\
& \left. - \frac{\vec{k}}{\hbar(\omega_{\vec{k}\pm\vec{p}}, \vec{k}\mp\omega)} \left(\frac{e^{iW_3 t/\hbar-1}}{W_3} \right) \right]
\end{aligned} \tag{93}$$

where the upper term in the bracket applies to phonon emission, the lower term applies to phonon absorption and

$$W_1 = \hbar(\omega_{\vec{k}\pm\vec{p}\pm\vec{q}, \vec{k}\mp\omega_q \mp \omega}) = E_{\vec{k}\pm\vec{p}\pm\vec{q}} - E_{\vec{k}} \mp E_q \mp \hbar\omega \tag{94}$$

$$W_2 = \hbar(\omega_{\vec{k}\pm\vec{q}\pm\vec{p}, \vec{k}\pm\vec{q} \mp \omega}) = E_{\vec{k}\pm\vec{q}\pm\vec{p}} - E_{\vec{k}\pm\vec{q}} \mp \hbar\omega \tag{95}$$

$$W_3 = \hbar(\omega_{\vec{k}\pm\vec{q}\pm\vec{p}, \vec{k}\pm\vec{p} \mp \omega_q}) = E_{\vec{k}\pm\vec{q}\pm\vec{p}} - E_{\vec{k}\pm\vec{p}} \mp E_q \tag{96}$$

The details of this derivation are presented in Appendix IV.

According to the usual perturbation methods, the transition probabilities are represented by the squares of the absolute values of the expansion coefficients. Thus, the probability per unit time that an electron initially in state \vec{k} will undergo a transition to any of the states $\vec{k} \pm \vec{p} \pm \vec{q}$ under the simultaneous influence of an external electromagnetic field and thermal lattice vibrations is

$$P(\vec{k} \rightarrow \vec{k} + \vec{q}) = \lim_{t \rightarrow \infty} \frac{1}{t} |a_{\vec{k} + \vec{q}}^{(2)}|^2 \quad (97)$$

The transition probability will approach a constant finite value for large t if and only if one or more of the denominator terms in Eq. (93) approaches zero for large values of t .

The transitions which involve simultaneous photon and phonon processes are represented by the energy relation given by Eq. (94). When the transition probabilities obtained from Eq. (93) are used in Eq. (53) to evaluate the energy expenditure of the field, the terms in W_2 and W_3 cancel. Therefore, it is sufficient to consider only the case when a singularity occurs at $W_1 = 0$. Accordingly we can reduce Eq. (93) to

$$a_{\vec{k} + \vec{q}}^{(2)} = + \frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \begin{Bmatrix} n_q \\ n_q + 1 \end{Bmatrix} \vec{E}_0 \cdot \left[\frac{\vec{k} + \vec{q}}{\hbar(\omega_{\vec{k} + \vec{q}}, \vec{k} + \vec{q})} + \frac{\vec{k}}{\hbar(\omega_{\vec{k}}, \vec{k})} \right] \frac{e^{iW_1 t / \hbar - 1}}{W_1} \quad (98)$$

For transitions in the visible and infrared portions of the spectrum the photon momentum can be neglected in comparison with either the electron momentum or the crystal momentum except in those terms which give rise to resonance. We can then write,

$$\vec{k}' = \vec{k} \pm \vec{p} \pm \vec{q} \approx \vec{k} \pm \vec{q}$$

It follows that

$$E_{k \pm p} = \frac{\hbar^2}{2m^*} (k \pm p)^2 = \frac{\hbar^2 k^2}{2m^*} \left(1 + \frac{p}{k}\right)^2 \approx \frac{\hbar^2 k^2}{2m^*} = E_k$$

Hence, terms such as $E_{k \pm p} - E_k$, which represent a relativistic correction, will be neglected in expressions which contain other additive energy terms. We shall let

$$B(q) = \pm \frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \quad (99)$$

Consider first the transition $\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}$. The parenthetical term in Eq. (98) becomes

$$\frac{\vec{k}(\omega_{k+p, k} + \omega_{k+q, k} - \omega_q - \omega) + \vec{q}(\omega_{k+p, k} - \omega)}{\hbar(\omega_{k+q, k} - \omega_q) (\omega_{k+p, k} - \omega)}$$

The coefficient of \vec{k} can be approximated by

$$E_{k+p} - E_k + E_{k+q} - E_k - \hbar\omega_q - \hbar\omega = E_{k+p} - E_k + W_1 \approx 0$$

where the term W_1 is taken as zero. Deviations of W_1 from zero remain important in the resonance term.

These simplifications reduce Eq. (98) for the transition $\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}$ to

$$a_{\vec{k}+\vec{p}+\vec{q}}^{(2)} = B(q) \sqrt{n_q} \frac{(\vec{E}_0 \cdot \vec{q})}{\hbar \omega} \frac{e^{iW_1 t / \hbar - 1}}{W_1} \quad (100)$$

Thus

$$P(\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}) = [B(q)]^2 n_q \frac{(\vec{E}_0 \cdot \vec{q})^2}{\hbar^2 \omega^2} \lim_{t \rightarrow \infty} \frac{1}{t} \left| \frac{e^{iW_1 t / \hbar - 1}}{W_1} \right|^2 \quad (101)$$

We can express this result in terms of the function $\delta(x)$ defined by Heitler (47)

$$\delta(x) = \lim_{t \rightarrow \infty} \frac{1}{2\pi t} \left| \frac{1 - e^{ixt}}{x} \right|^2$$

Thus

$$P(\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}) = \frac{2\pi}{\hbar^3 \omega^2} [B(q)]^2 n_q (\vec{E}_0 \cdot \vec{q})^2 \delta(W_1) \quad (102)$$

This can be generalized to include the other processes as

$$P(\vec{k} \rightarrow \vec{k}' + \vec{p} + \vec{q}) = \frac{2\pi}{\hbar^3 \omega^2} [B(q)]^2 \begin{Bmatrix} n_q \\ n_q + 1 \end{Bmatrix} (\vec{E}_0 \cdot \vec{q})^2 \quad (103)$$

$$\cdot \delta(E_k, -E_{k'} - \hbar\omega_q - \hbar\omega)$$

where we have denoted the final electron state as \vec{k}' .

Substituting Eq. (103) into Eq. (51) yields

$$P_r^s(\vec{k}) = \sum_{\vec{k}'} \frac{4\pi}{\hbar^3 \omega^2} B(q)^2 \begin{Bmatrix} n_q \\ n_q + 1 \end{Bmatrix} (\vec{E}_0 \cdot \vec{q})^2 \quad (104)$$

$$\cdot [1 - g(E_{k'})] \delta(E_k, -E_{k'} - \hbar\omega_q - \hbar\omega)$$

The summation over the final states can be replaced by the corresponding integral over k -space. Furthermore, because $\vec{k}' \approx \vec{k} + \vec{q}$, the summation over \vec{k}' is equivalent to a summation over \vec{q} . Thus the wave vector sum can be converted to an integral by (38)

$$\sum_{\vec{k}'} \rightarrow \sum_{\vec{q}} \rightarrow \frac{1}{(2\pi)^3} \iiint d^3\vec{q}$$

The wave vector element can be written (31)

$$d^3\vec{q} = q^2 dq d\Omega = q^2 dq \sin \gamma d\gamma d\phi. \quad \text{Because we have assumed a spherical}$$

Fermi surface, the energy relations are spherically symmetric. If we

also take the average field direction with respect to the phonon wave vector, we can write

$$\overline{(\vec{E}_0 \cdot \vec{q})^2} = \frac{1}{3} q^2 E_0^2$$

We can then express Eq. (104) as (see Appendix IV)

$$P_r^s(\vec{k}) = \frac{E_0^2}{6\pi^2 \hbar^3 \omega^2} \int_0^{2\pi} d\phi \int_0^{q_{\max}} q^4 dq \int_{-1}^{+1} [E(q)]^2 \begin{Bmatrix} n_q \\ n_{q+1} \end{Bmatrix} \quad (105)$$

$$\cdot d(\cos \gamma) [1-g(E_k)] \delta(E_k - E_k + \hbar\omega_q + \hbar\omega)$$

where γ is the angle between \vec{k} and \vec{q} .

The maximum phonon wave vector is determined by the phonon dispersion. We shall adopt the familiar Debye distribution for which the maximum wave vector is related to the longitudinal acoustic phase velocity v_a by (36)

$$q_{\max} = \frac{K\theta}{\hbar v_a} \quad (106)$$

where θ is the characteristic Debye temperature.

We can express the argument of the δ -function in Eq. (105) as

$$\begin{aligned}
 E_{\mathbf{k}'} - E_{\mathbf{k}} + \hbar\omega_{\mathbf{q}} + \hbar\omega &\approx \frac{\hbar^2 |\mathbf{k} + \mathbf{q}|^2}{2m^*} - \frac{\hbar^2 k^2}{2m^*} + \hbar\omega_{\mathbf{q}} + \hbar\omega \\
 &\approx \frac{\hbar^2 q^2}{2m^*} + \frac{\hbar^2 kq}{m^*} \cos \gamma + \hbar\omega_{\mathbf{q}} + \hbar\omega
 \end{aligned}$$

It follows from Eq. (101) that finite transition probabilities occur only when the argument of the δ -function vanishes. Wilson (36) has established the existence of a real $\cos \gamma$ such that the argument vanishes for all phonon wave vectors between zero and q_{\max} when no external field is present. A more general argument, applicable to the case of a perturbing field, is presented in Appendix IV. If we utilize this feature of the electron-phonon interaction to perform the integration over $\cos \gamma$ (see Appendix IV), Eq. (105) becomes

$$P_r^s(\mathbf{k}) = \frac{eE_d^2 E_0^2}{24\pi\hbar^2 m^* k\omega^4} \int_0^{q_{\max}} q^5 \left(\frac{1}{\rho_p \omega_{\mathbf{q}}} \right) \left\{ \begin{matrix} n_{\mathbf{q}} \\ n_{\mathbf{q}} + 1 \end{matrix} \right\} [1 - g(E_{\mathbf{k}} + \hbar\omega_{\mathbf{q}} + \hbar\omega)] dq \quad (107)$$

The average value of this transition probability is obtained as in Eq. (52),

$$\overline{P_r^s} = \frac{\sum_{\mathbf{k}'} g(E_{\mathbf{k}'}) P_r^s(\mathbf{k}')}{\sum_{\mathbf{k}'} g(E_{\mathbf{k}'})} \quad (108)$$

We shall assume that the visible and infrared transitions occur near the Fermi level because it is only at this energy level that close-by unoccupied states are available. Hence, the numerator of Eq. (108) is different from zero only when $E_k \approx E_f$, the Fermi energy. The summations over the initial electron states can be replaced with energy integrals and the density of states can be approximated by the value at the Fermi level. The average transition probability then becomes (see Appendix IV)

$$\overline{p_r^s} = \frac{e^2 E_d^2 E_0^2}{32\pi^2 m^* \hbar \omega^4 E_f} \int_0^{q_{\max}} \frac{1}{\rho_p \omega_q} \begin{Bmatrix} n_q \\ n_q + 1 \end{Bmatrix} dq \cdot \frac{1}{\beta} \int_{-\infty}^{\infty} \frac{e^z dz}{(e^{z+a} + 1)(e^z + 1)} \quad (109)$$

where

$$\beta = 1/KT$$

$$z = \beta (E_k - E_k \mp \hbar \omega_q \pm \hbar \omega)$$

$$a = \beta (\mp \hbar \omega_q \mp \hbar \omega)$$

The energy integral can be evaluated in closed form,

$$K_r^s = \frac{1}{\beta} \int_{-\infty}^{\infty} \frac{e^z dz}{(e^{z+a}+1)(e^z+1)} = \frac{a}{\beta(e^a-1)} \quad (110)$$

Then, from Eq. (53), the power expenditure of the external field is

$$W(\omega, T) = \frac{e^2 E_d^2 E_0^2}{32\pi h m^* k \omega^3 E_F} \sum_s \int_0^{q_{\max}} q^5 \left(\frac{1}{\rho_p \omega q} \right) \begin{Bmatrix} n_q \\ n_q + 1 \end{Bmatrix} dq [K_a^s - K_e^s] \quad (111)$$

Substituting from Eq. (110) we have, after considerable algebraic manipulation (see Appendix IV),

$$W(\omega, T) = C_0 \frac{E_0^2}{8\pi N} \left(\frac{\omega_p}{\omega} \right)^2 \left(\frac{T}{\theta} \right)^5 J(\omega, T) \quad (112)$$

where

$$J(\omega, T) = \frac{(e^{2\eta}-1)}{2\eta} F_5(\eta, \zeta) - \frac{1}{2} (e^{\eta}-1)^2 F_4(\eta, \zeta) - (e^{\eta}-1)^2 G_4(\eta, \zeta) \quad (113)$$

$$F_n(\eta, \zeta) = \int_0^{\zeta} \frac{x^n dx}{(e^x - e^{\eta})(e^{\eta} - e^{-x})} \quad (114)$$

$$G_n(\eta, \zeta) = \int_0^{\zeta} \frac{x^n dx}{(e^x - e^{\eta})(e^{\eta} - e^{-x})(e^x - 1)} \quad (115)$$

$$\eta = \frac{h\nu}{kT} ; \quad \zeta = \frac{\theta}{T} \quad (116)$$

and C_0 is a constant which is independent of both frequency and temperature,

$$C_0 = \frac{9\pi^3 \hbar^2 N_p E_d^2}{2 \sqrt{2m^* E_F^3} MK\theta} \quad (117)$$

The Electron-Phonon Damping Coefficient

The optical conductivity is defined as the energy absorbed per unit volume per unit time divided by the mean square of the electric field vector (37)

$$\sigma(\omega) = \frac{2NW}{E_0^2} \quad (118)$$

where $E_0^2/2$ is the field energy density and N is the effective number of electrons. Substituting for W from Eq. (112), we have

$$\sigma(\omega, T) = \frac{1}{4\pi} C_0 \left(\frac{\omega_p}{\omega} \right)^2 \zeta^{-5} J(\omega, T) \quad (119)$$

The term $C_0 \zeta^{-5} J(\omega, T)$ has the units of sec.^{-1} and can be conveniently interpreted as a damping coefficient. Furthermore, we note from Eq. (113) that

$$\lim_{\omega \rightarrow 0} J(\omega, T) = \int_0^{\zeta} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} = F_5^0(\zeta) \quad (120)$$

which is the integral which appears in the Bloch-Grüneisen relation for dc conductivity (39). Thus, if we define a quantum correction factor for the electron-phonon interaction as

$$Q(\eta, \zeta) = \frac{J(\eta, \zeta)}{F_5^0(\zeta)} \quad (121)$$

such that

$$\lim_{\omega \rightarrow 0} Q(\eta, \zeta) = 1$$

then we can formulate the electron-phonon damping coefficient as

$$\Gamma(\eta, \zeta) = C_0 \zeta^{-5} F_5^0(\zeta) Q(\eta, \zeta) = \Gamma^0(\zeta) Q(\eta, \zeta) \quad (122)$$

If this relation is used in Eq. (34) and taken to the dc limit of zero frequency, we have

$$\sigma_0 = \lim_{\omega \rightarrow 0} \sigma(\omega, T) = \lim_{\omega \rightarrow 0} \frac{Ne^2}{m^*} \left(\frac{\Gamma}{\omega^2 + \Gamma^2} \right) = \frac{Ne^2}{m^* \Gamma_0}$$

which is the familiar relation for dc conductivity where $\Gamma_0(\zeta)$ is the dc damping coefficient.

We shall be interested in the application of this theory for temperatures between room temperature and the melting temperature of the particular metal and for frequencies in the range of interest in thermal radiation analysis, that is, for wavelengths between about 0.5 and 100 microns which corresponds to an angular frequency range of about 4.7×10^{15} to 1.9×10^{13} sec.⁻¹. The frequencies greater than about 2×10^{14} sec.⁻¹ are of particular interest because it is at such frequencies that significant deviations from the Hagen-Rubens formula are observed. The corresponding ranges of the independent variables η and ζ are shown in Figure 8.

Several digital computer subprograms were developed to evaluate the various mathematical functions which appear in the theory. These subprograms were later used as external routines in the program for the calculation of emissivity and are discussed in Appendix V. The function $F_5^0(\zeta)$, as defined by Eq. (120), is familiar from dc conductivity theory. The curve shown in Figure 9 was obtained using a numerical integration with Simpson's rule. The values can be compared with tabulations from the literature (40).

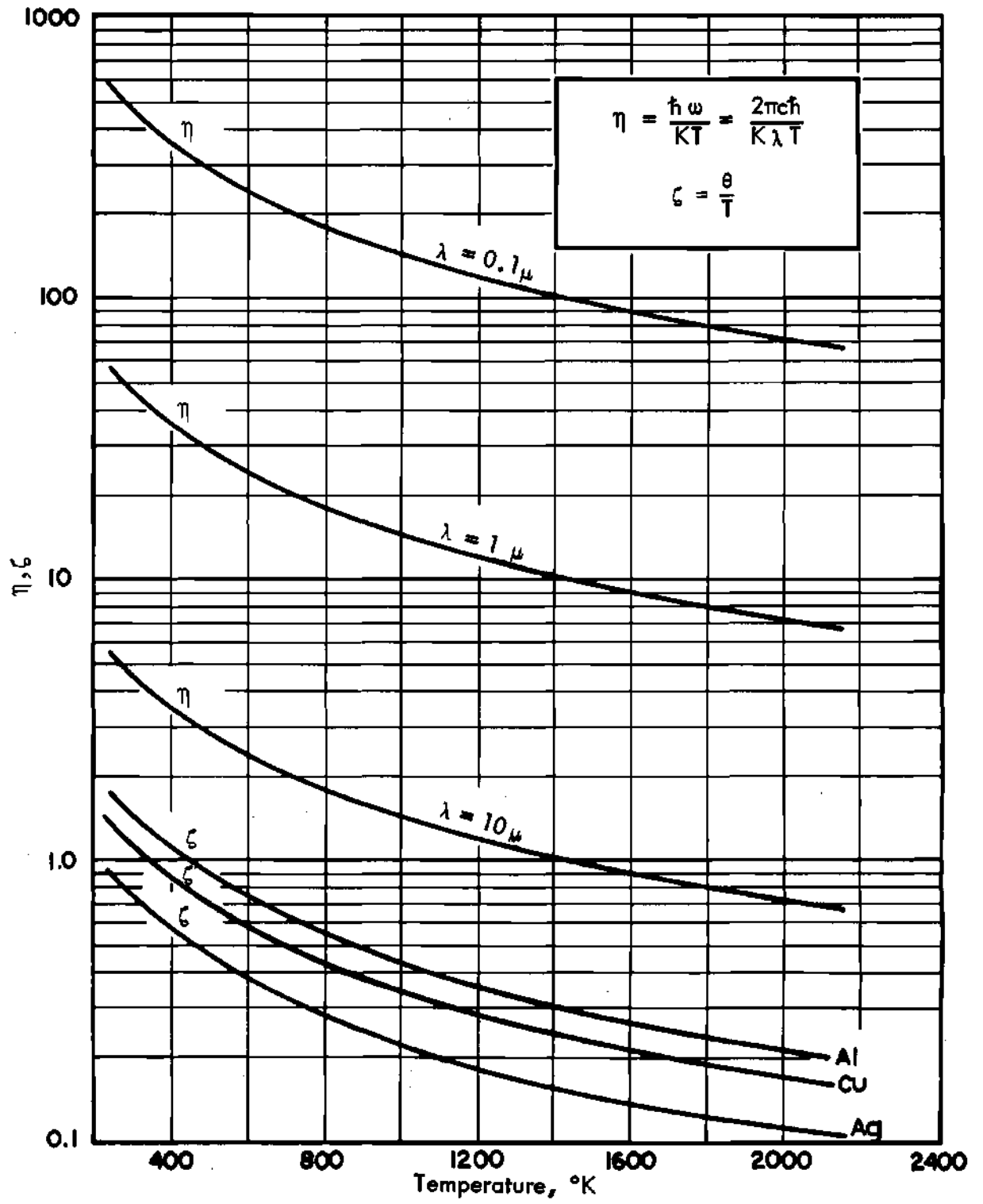
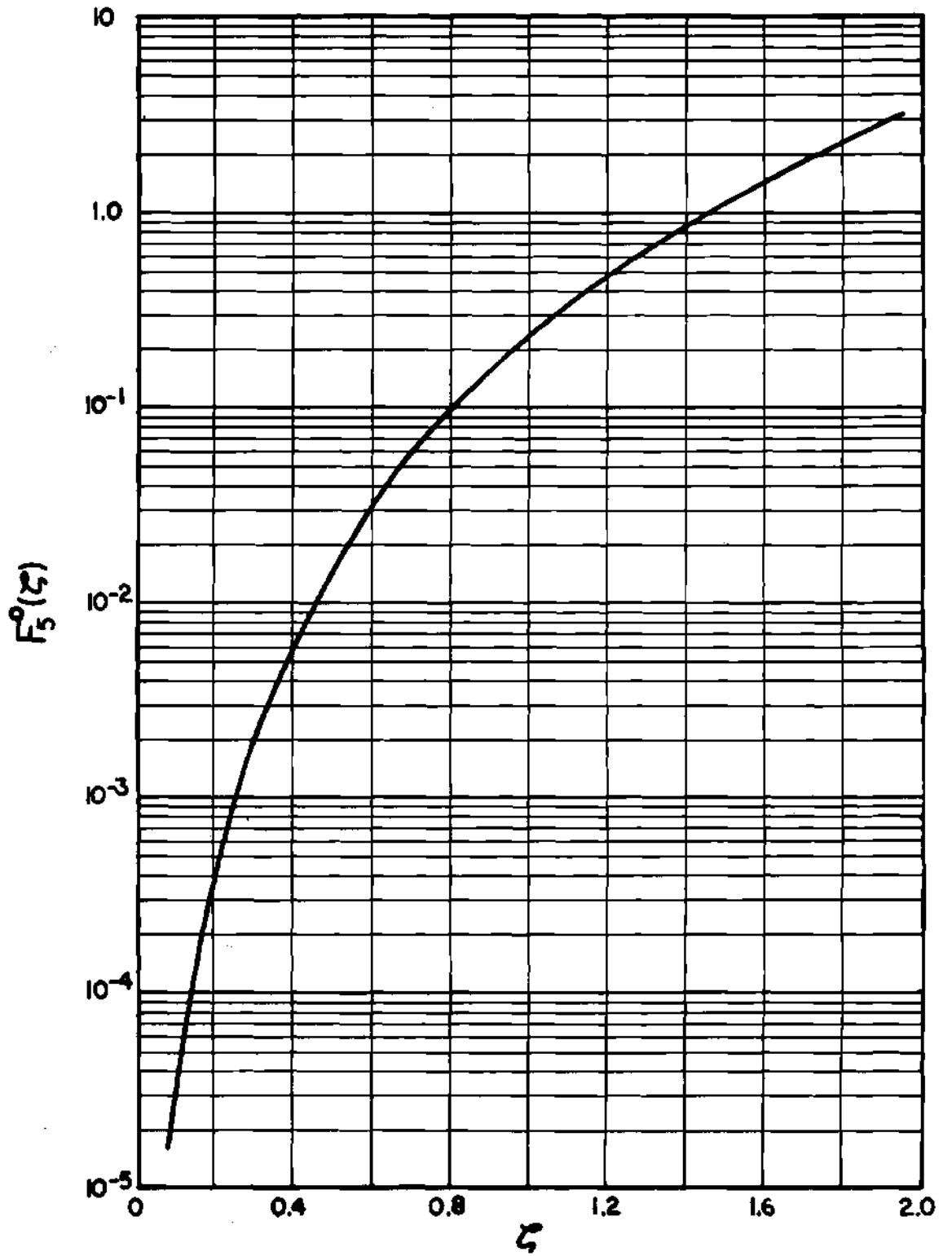


Figure 8. Range of Independent Variables η and ζ

Figure 9. The Function $F_5^0(\zeta)$

The electron-phonon quantum correction factor $Q(\eta, \zeta)$ represents the degree to which the quantum effects included in the model cause a change in the electron damping coefficient. It can be seen from Eq. (122) that when $Q(\eta, \zeta)$ is unity the damping coefficient corresponds to the dc case and the relation for conductivity reduces to the Bloch-Grüneisen relation. Although the latter is a consequence of an elementary quantum analysis, it represents only a limiting case, that is, the zero-frequency limit. The functions $F_n(\eta, \zeta)$ and $G_n(\eta, \zeta)$ were evaluated with subprograms which utilize Simpson's rule for integration. These routines and the subprogram for $F_5^0(\zeta)$ were used in a program to evaluate the electron-phonon quantum correction factor. The results are shown in Figure 10 where the quantity $1-Q(\eta, \zeta)$ is plotted as a function of ζ for different values of η . It can be seen that $1-Q(\eta, \zeta)$ is much more sensitive to temperature than to frequency. It increases by three orders of magnitude as ζ goes from 0.1 to 3. On the other hand, it increases only 40 to 50 per cent as η increases from 10 to 1000. Because the dc damping coefficient $\Gamma^0(\zeta)$ is, of course, independent of frequency, the electron-phonon damping coefficient, given by Eq. (122) is only slightly dependent on frequency, that dependence arising solely from the quantum correction factor.

The constant C_0 , defined by Eq. (117), is a function of the microscopic parameters of the metal. It involves the Debye temperature θ ,

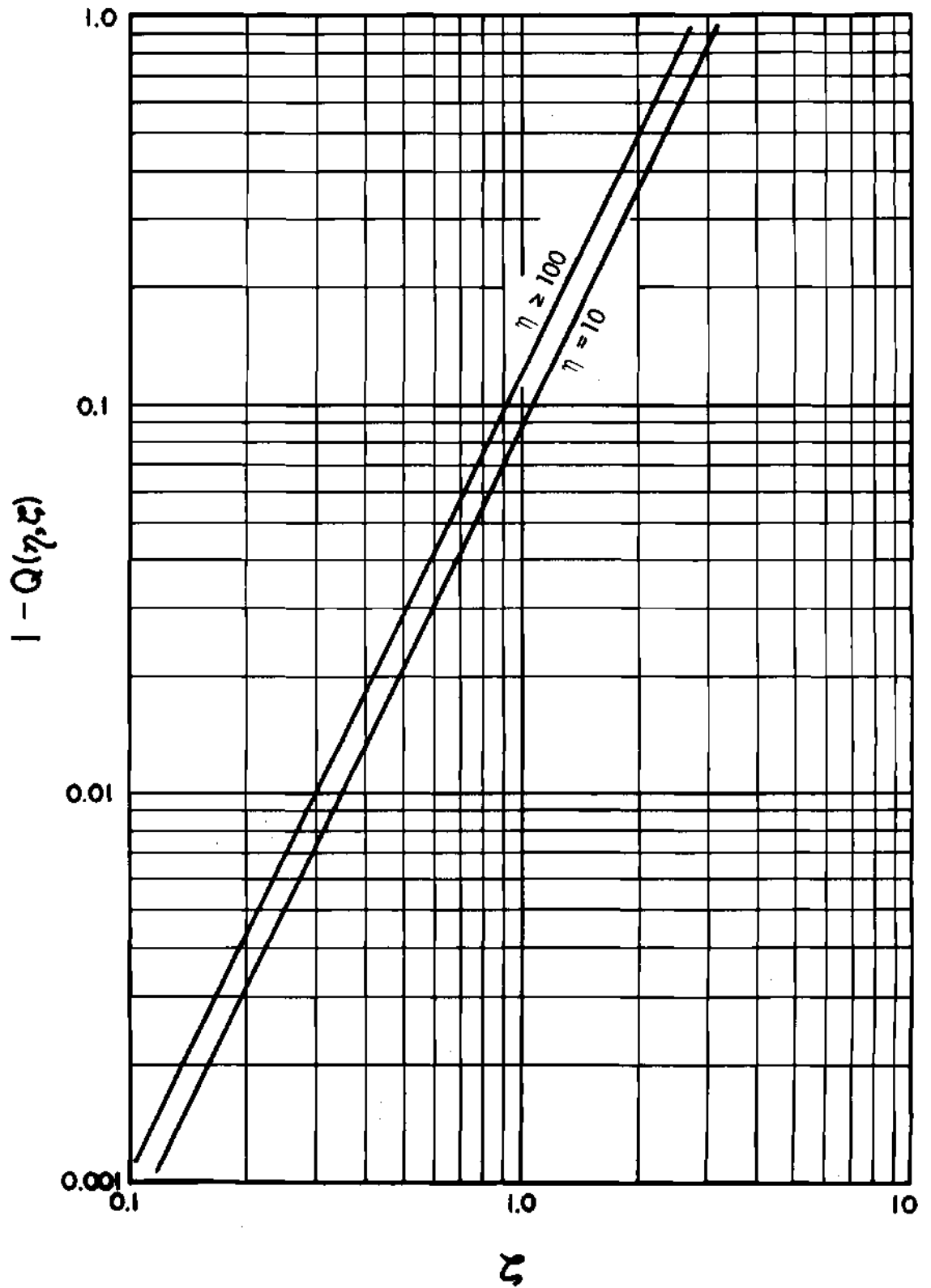


Figure 10. The Electron-Phonon Quantum Correction Factor

the ionic mass M , the electron effective mass m^* , the Fermi energy E_f and the deformation potential energy term E_d . The evaluation of this constant from first principles is complicated by the lack of accurate data on the microscopic parameters. Although the ionic mass, Fermi energy and Debye temperature are known with reasonable accuracy for a variety of metals, effective mass data are available for only a few metals and almost no values of E_d are given in the literature. There is, however, a convenient indirect method by which C_0 can be evaluated. From Eq. (122) we can write

$$C_0 = \zeta^5 \frac{\Gamma^0(\zeta)}{F_5^0(\zeta)}$$

We can then use Eq. (36) to express the dc damping coefficient in terms of the dc conductivity; hence

$$C_0 = \zeta^5 \frac{Ne^2}{m\sigma_0 F_5^0(\zeta)} = \frac{(\hbar\omega_p)^2}{4\pi\hbar^2} \left(\frac{1}{\sigma_0}\right) \frac{\zeta^5}{F_5^0(\zeta)} \quad (123)$$

The term $\hbar\omega_p$ is the plasmon energy of the metal. Values of $\hbar\omega_p$ extracted from the literature are tabulated in Appendix I. Experimental values of the dc conductivity and the plasmon energy can be used in Eq. (123) to evaluate C_0 where ζ and $F_5^0(\zeta)$ are evaluated for the temperature at which σ_0 and $\hbar\omega_p$ were measured. The results are listed for several metals in Appendix I.

The damping coefficient which appears due to the electron-phonon interaction is plotted as a function of temperature in Figure 11 for copper and silver. The curves apply for the wavelength range from 0.1 to 10 microns for which the dependence on wavelength is very slight.

The Electron-Electron Interaction

One of the assumptions employed in the preceding theoretical formulation was that the contribution of the mutual electron interactions to the total electron damping coefficient was small compared with that of the electron-phonon interactions. This is not always the case. The total damping coefficient Γ_T can be expressed as the sum of the electron-phonon damping coefficient Γ , the electron-electron damping coefficient Γ_e , and the electron-impurity damping coefficient Γ_i ,

$$\Gamma_T(\eta, \zeta) = \Gamma(\eta, \zeta) + \Gamma_e(\eta, \zeta) + \Gamma_i \quad (124)$$

It was previously assumed that, because the mean free path for electron-electron collisions in a free electron gas was much larger than the mean free path for electron-phonon collisions, then $\Gamma_e \ll \Gamma$. This enabled us to obtain a perturbation solution of the Schroedinger equation and arrive at the relation for the electron-phonon damping coefficient. Indeed, if only normal electron transitions (N-processes) are considered, the electron-electron interaction cannot contribute to the electrical

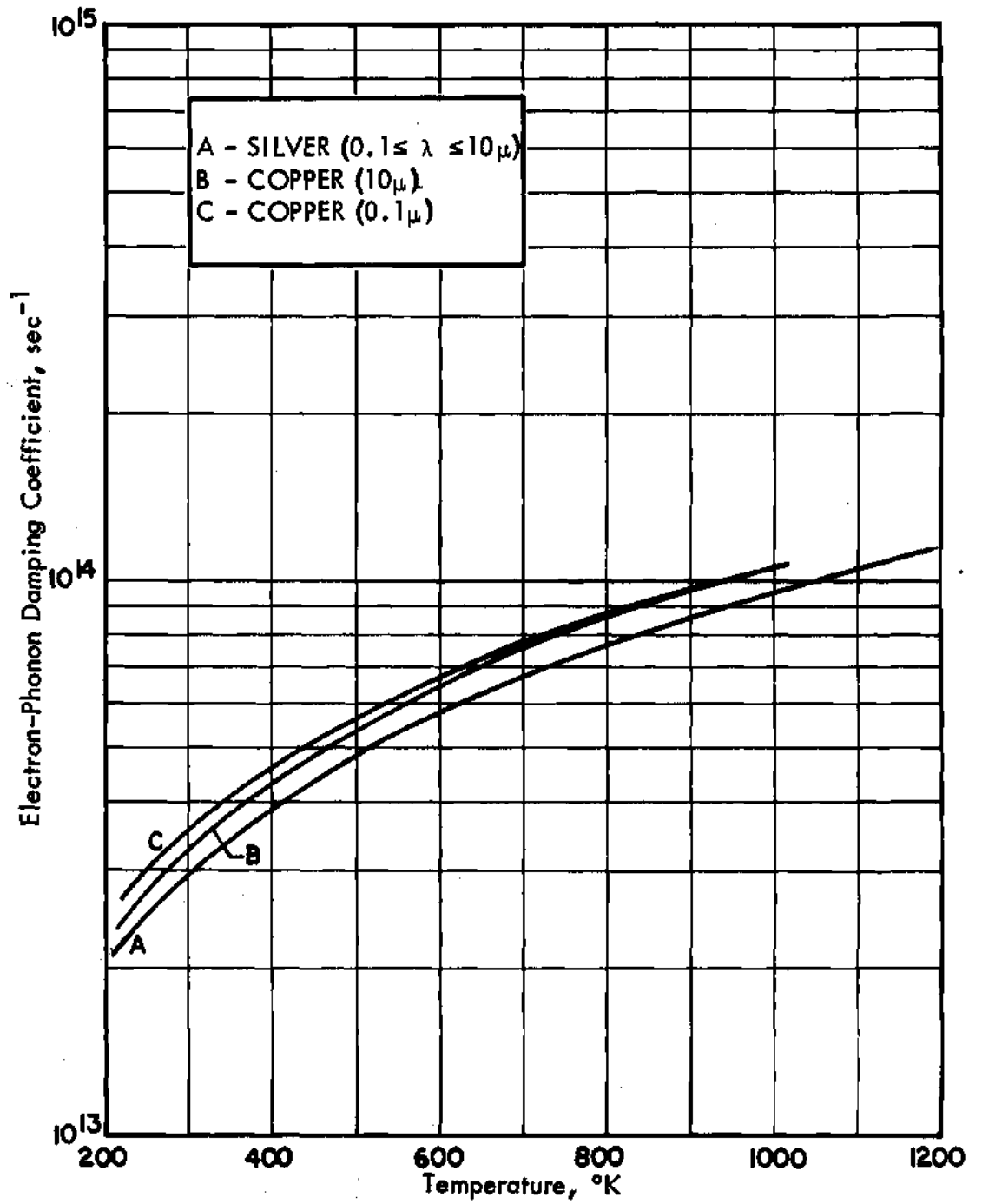


Figure 11. Electron-Phonon Damping Coefficient of Silver and Copper

resistivity because no momentum can be transferred to the crystal lattice as a result of such collisions (40). However, if Umklapp processes (U-processes) are considered, the lattice can exchange momentum with the electrons due to mutual electron interaction.

The electron-electron interaction was ignored in most early quantum studies of the optical properties of metals. More recently, however, the effect of interelectronic collisions on the electrical conductivity has been studied by Ginzburg and Silin (48), Silin (49), Gurzhi (50) and Appel (51). The work of Silin and of Gurzhi was based on the theory of Fermi liquids. There remains considerable controversy over the importance of the electron-electron interaction. However, we shall find that, as it is formulated in the present theory, it can make a significant contribution to the overall damping coefficient.

We shall not treat mutual electron interactions in detail. Instead we shall employ the relation presented by Gurzhi (50) for the electron-electron damping coefficient.

$$\Gamma_e(\eta, \zeta) = \Gamma_e^0(\zeta) \left[1 + \left(\frac{\eta}{2\pi} \right)^2 \right] \quad (125)$$

where $\Gamma_e^0(\zeta)$ is the classical electron-electron collision frequency which is known to be proportional to T^2 (35). Hence, the term $1 + (\eta/2\pi)^2$ can be regarded as an electron-electron quantum correction factor. The damping coefficient $\Gamma_e(\eta, \zeta)$ increases with increasing temperature and

with increasing frequency. The frequency dependence enters only in the quantum correction term.

The classical damping term can be written

$$\Gamma_e(\zeta) = C_e(\zeta)^{-2} \quad (126)$$

where C_e is a constant characteristic of a given metal but independent of both frequency and temperature. Very little experimental data is available concerning the term $\Gamma_e^0(\zeta)$. Padalka and Shklyarevskii (52) report values for silver and gold. These were used to obtain the values of C_e for silver and gold listed in Appendix I. The following relation (48) was used to estimate $\Gamma_e(\zeta)$ for other metals,

$$\Gamma_e^0(\zeta) = \frac{v_f}{l_e} \approx S_e N \left(\frac{KT}{E_f} \right)^2 v_f \quad (127)$$

or

$$C_e \approx S_e N \left(\frac{KT}{E_f} \right)^2 v_f \quad (128)$$

where l_e is the mean free path between electron-electron collisions and S_e is the effective collision cross-section which was assumed to be 10^{-15} cm^2 (9). The most complete data on the number of conduction

electrons per unit volume N and the electron velocity at the Fermi level v_f appears to be that of Dingle (53) (see Appendix I).

The Electron-Impurity Interaction

Electron-impurity interactions include all forms of electron scattering by stationary crystal imperfections. The impurity damping coefficient is a result of electron interactions with not only impurity atoms but also planar imperfections such as grain boundaries and stacking faults, linear imperfections such as edge and screw dislocations and other point imperfections such as vacancies and interstitial atoms. The boundaries of a metallic specimen can also be regarded as planar imperfections; however, we shall qualitatively account for the effect of surface potentials when we discuss skin effects in a later section. A summary of stationary crystal imperfections and related scattering mechanisms in metals is presented by Blatt (40).

The difficulties encountered in any attempt to analytically describe electron damping by stationary crystal imperfections are obvious. The mechanisms are many and complex; furthermore, such damping will depend on the purity of the metal and the manner in which a specimen is prepared. Matthiessen's rule, Eq. (47), indicates that the residual resistivity and, therefore, the impurity damping coefficient are independent of temperature. Hence, an estimate of the impurity damping

coefficient can be obtained from measured values of the residual resistance because, according to Mott and Jones (37),

$$\rho_0 = \frac{m^*}{Ne^2} \Gamma_i = \frac{\omega_p^2}{4\pi} \Gamma_i \quad (129)$$

Thus

$$\Gamma_i = \frac{4\pi}{\omega_p^2} \rho_0 \quad (130)$$

The values of Γ_i for silver and gold have been measured experimentally (52) and are listed in Appendix I. The other values listed were computed from Eq. (130) using the residual resistivity data compiled by Meaden (54).

The values of C_e and Γ_i computed for silver and gold using Eqs. (128) and (130) are appreciably smaller than the experimental values obtained by Padalka and Shklyarevskii (52). This would indicate that the free-electron theory underpredicts both C_e and Γ_i ; that is, the effects of mutual electron collisions and impurity interactions are somewhat greater than predicted by classical theory. More accurate estimates of C_e and Γ_i could be obtained by fitting the present theory to room-temperature values of the optical properties. The constants could then be used to predict the thermal radiation properties at other temperatures. This means of determining C_e and Γ_i is discussed in the next chapter.

The Bulk Absorptivity

The theory, subject to its many assumptions and qualifications, can now be applied to the theoretical calculation of the bulk absorptivity, or bulk emissivity, of metals. The electron-phonon damping coefficient can be obtained from Eq. (122) and the electron-electron damping coefficient from Eq. (125). These are added to the constant electron-impurity damping coefficient to obtain the overall damping coefficient, Eq. (124), which is a function of both temperature and frequency. This is then used in Eqs. (34) and (35) to determine the optical conductivity and the dielectric constant. The optical constants n and k are given by Eqs. (17) and (18) and are used in Eq. (24) to find the normal monochromatic bulk absorptivity (or emissivity). Theoretical calculations are presented and discussed in Chapter IV.

Skin Effects

The bulk absorptivity α_b accounts for the internal processes such as the electron-phonon, electron-electron and electron-impurity interactions. It does not, however, include skin effects which account for the interaction of the conduction electrons with the surface potential. It is common practice to express the absorptivity of an opaque solid as the sum of the bulk absorptivity and a skin absorptivity α_s ,

$$\alpha(\omega, T) = \alpha_b(\omega, T) + \alpha_s \quad (131)$$

The formal theory of the skin effect was developed by Reuter and Sondheimer (55) and Dingle (56). We shall not present a detailed account of the theory; rather, we shall utilize the familiar first-order relation for the skin absorptivity (41),

$$\alpha_s = \frac{3}{4} \frac{v_f}{c} \quad (132)$$

where v_f is the electron velocity at the Fermi level which is given by (9)

$$v_f = \frac{\hbar}{m^*} (3\pi^2 N)^{1/3} \quad (133)$$

The values of v_f/c given in Appendix I are mostly those reported by Dingle (53). The relation for the skin absorptivity, Eq. (132), is the final requirement in the theory. We are now in a position to compute the optical properties and emissivity of a metal as functions of temperature and wavelength. The computational results for several metals and their comparison with available experimental data are presented and discussed in the next chapter.

CHAPTER IV

EVALUATION AND APPLICATION OF THE THEORY

The theory developed in the preceding chapter might be categorized as a modified free-carrier theory of absorption and emission. It retains several of the features of free-electron theory, notably the assumption of a spherical Fermi surface. However, it includes modifications such as the concept of effective mass and the qualitative electron-electron and electron-impurity interaction terms. In this chapter we shall assess the theory by computing values of the damping coefficient, index of refraction, extinction coefficient and normal monochromatic emissivity and by comparing the results with experimental data. We shall also discuss in more detail the limitations of the theory which determine the metals to which it can be applied and the temperature and frequency ranges over which it remains reasonably valid.

In the development of the theory we have assumed that the Fermi surface is spherical and that no interband transitions occur. These are the most far-reaching assumptions of the theory. We know that the Fermi surface is truly spherical only for a free-electron Fermi gas. However, we also know that the assumption of a spherical Fermi surface has been used with considerable success in the theory of the electrical properties

of many metals, particularly the alkali and noble metals. At a temperature above absolute zero the width of the rapidly varying part of the Fermi distribution is approximately kT as shown in Figure 12. Unoccupied electron states are thus available within a range kT about the Fermi level. An electron can absorb a photon only if the photon energy $h\nu$ is sufficient to raise the electron to a higher unoccupied state. Thus if $h\nu \geq kT$, quantum absorption can occur in the free-electron gas. If $h\nu \ll kT$, as would be the case in the far infrared, the electrons absorb electromagnetic energy only as a result of their acceleration in the field. This explains the limitations of a classical analysis of absorption to the long-wavelength and/or high-temperature regions. Noland (24) has demonstrated that the region over which the Hagen-Rubens formula is valid extends to shorter wavelengths as temperature is increased.

A convenient measure of the validity of the assumption of a spherical Fermi surface is the degree to which the valence electrons of a specific metal can be approximated by a free-electron gas. A qualitative estimate of this can be obtained from the electronic structure of the metal. The monovalent alkali metals have a single electron in an s-state outside a complete closed shell. It would be expected, therefore, that they might exhibit certain features characteristic of the free-electron model. The monovalent noble metals, Cu, Ag and Au, also have a single s-state electron outside a complete shell; however, in this case,

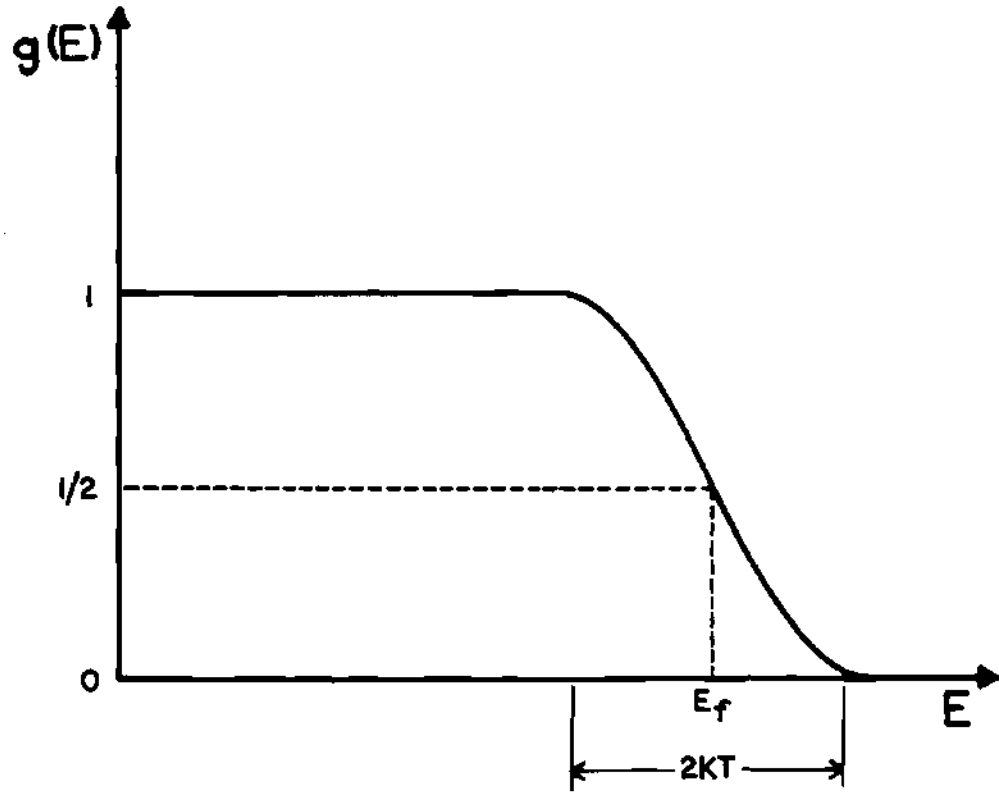


Figure 12. The Fermi-Dirac Distribution

the d-electrons of the complete shell form a band which overlaps the s-band. Although available evidence (39) indicates that the Fermi surfaces of the noble metals deviate from a spherical shape, their electronic structure is such that the outer s-state electrons would be expected to conform with reasonable accuracy to a free-electron model. The alkali metals are rarely used as surfaces in thermal radiation systems and, hence, we shall treat them only from the viewpoint of verification of the theory. The noble metals, however, are important in many engineering systems and will be studied in detail.

Aluminum is another important metal which is frequently used in thermal radiation systems, particularly for aeronautic and space applications. It is the only one of the trivalent metals which has been studied in detail. It is a good electrical conductor and the general topology of the Fermi surface closely approximates a sphere (39).

Another very important class of engineering metals are the transition metals. The first group, V, Cr, Mn, Fe, Co and Ni, have an argon core configuration plus electrons in the 3d and 4s shells. The second group, Nb, Mo, Tc, Ru, Rh and Pd, have a krypton core configuration plus electrons in the 5d and 6s shells. Because the d-shells are incomplete, the d-state electrons can influence many of the properties of the transition metals. The complexity of the d-states makes it very difficult to obtain reliable information concerning the Fermi surface.

Certainly the shape of the surface would be expected to deviate considerably from spherical and the free-electron model would be a poor representation of the transition elements.

However, our theory is not strictly a "free-electron theory" in the exclusive sense of that terminology. We have attempted to improve on the free-electron model by including terms to account, at least qualitatively, for such factors as electron-electron interactions and skin effects. We might, therefore, expect better agreement with experimental data than if we had developed a truly free-electron theory. Correlation of data for the transition metals, however, is limited by our restriction of the theory to intraband transitions. In the case of the alkali and noble metals, if $\hbar\omega \gtrsim kT$, states are available for transitions within the s-band and at energies near the Fermi level. Relatively large photon energies would be required to cause a transition from the d-band to the s-band in the noble metals. In the transition metals, however, interband absorption can occur at frequencies of interest in thermal radiation because of the relatively small photon energy required to cause a $d \rightarrow s$ transition.

We shall evaluate the theory by comparing the computed results with experimental data for several metals. We shall treat sodium as typical of the alkali metals and present the results only as an indication of the accuracy of the theory since the alkali metals are of limited engineering value in thermal radiation systems. Copper, silver and gold

will be treated in detail. Aluminum will be analyzed to further assess the limitations of the theory. Nickel will be treated as characteristic of the transition metals mainly as a means of illustrating the possible modifications required to account for interband transitions. In each case the specific limitations of the theory will be discussed.

The Alkali Metals

The alkali metals, Li, Na, K, Rb and Cs, have the least complicated electronic structure of all the metallic elements and should most closely conform to the free-electron model. Because of their chemical reactivity and softness, they are rarely used as thermal radiation surfaces and, therefore, are only of academic interest to this study. It is worthwhile, however, to assess the ability of the theory to predict the optical properties of the alkali metals because we would expect the atomic model to be most applicable to these metals. We select sodium as typical of the alkali metals and use the atomic parameters given in Appendix I to compute the optical and thermal radiation properties.

The optical conductivity of sodium at room temperature is presented in Figure 13. The theoretical values are in good agreement with the experimental data of Hodgson (57) and slightly higher than the data of Mayer and Heitel (58) for wavelengths greater than about one micron. At wavelengths less than one micron the data seem to indicate resonance phenomena; that is, the energy of the field is sufficient to excite bound

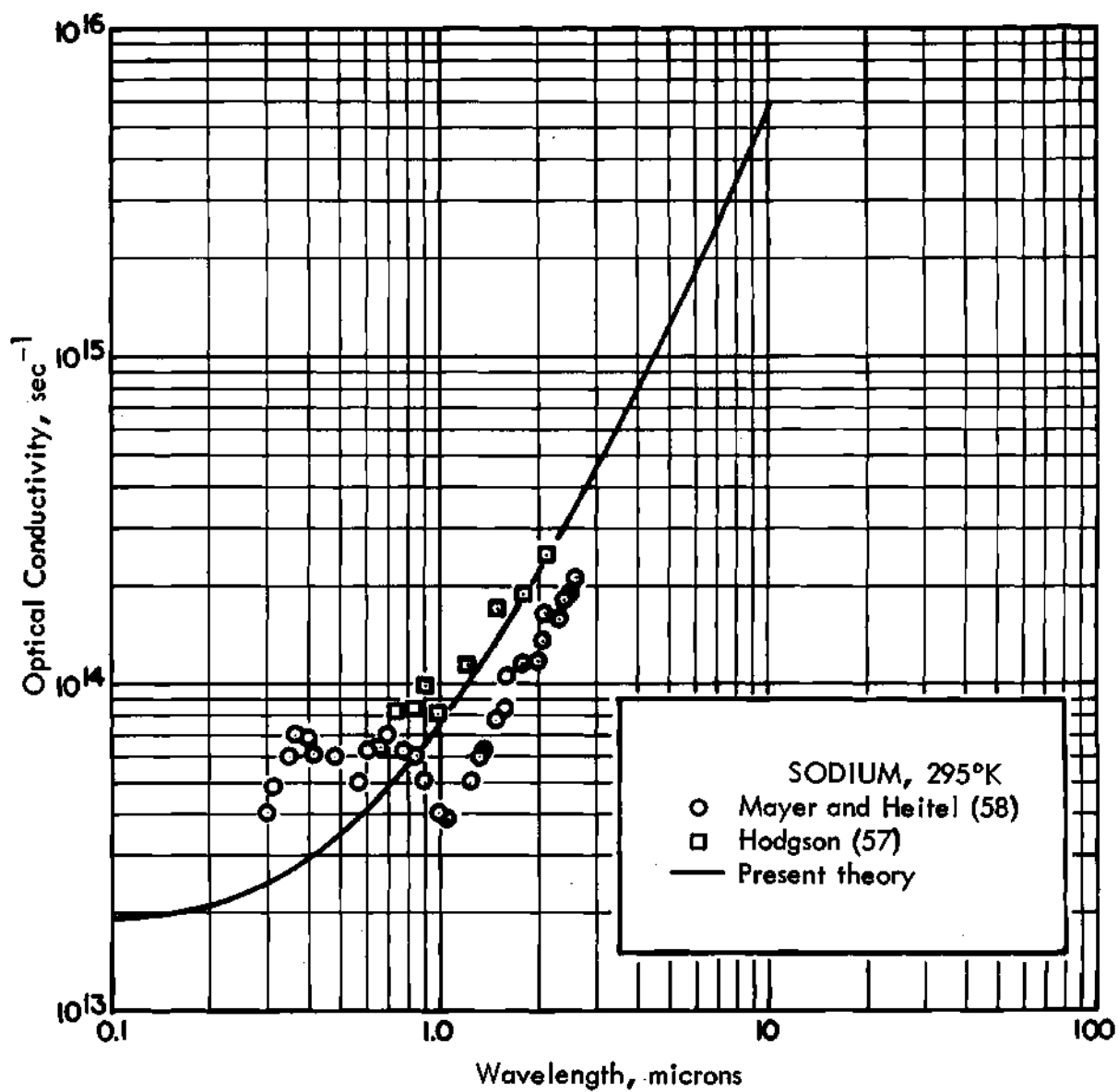


Figure 13. Optical Conductivity of Sodium at Room Temperature

electrons in the 2p shell and interband transitions probably occur. A theory which accounts only for intraband free-electron transitions would yield a straight line in Figure 13. In the present theory the shape of the curves at short wavelengths is strongly influenced by the electron-electron interaction term which we have chosen in Eq. (125). This important observation holds for each of the metals which we shall study and will be discussed in more detail later in this chapter.

Hodgson (57) finds that the onset of interband transitions in sodium occurs at a photon energy of 1.2 ev. This corresponds to a wavelength of 1.03 microns and serves as an indication of the lower wavelength limit of application of a theory restricted to intraband transitions. The present theory, however, does exhibit structure at shorter wavelengths, although not exactly of the nature required for the interband transitions.

The optical properties of sodium are shown in Figure 14. Unfortunately, very little experimental data exist for wavelengths in the near infrared. Theoretical values of the emissivity at room temperature are plotted in Figure 15. Because the alkali metals are not used as thermal radiation surfaces, no experimental emissivity data are available. The theoretical curve indicates the marked increase in emissivity at wavelengths less than one micron caused by quantum absorption.

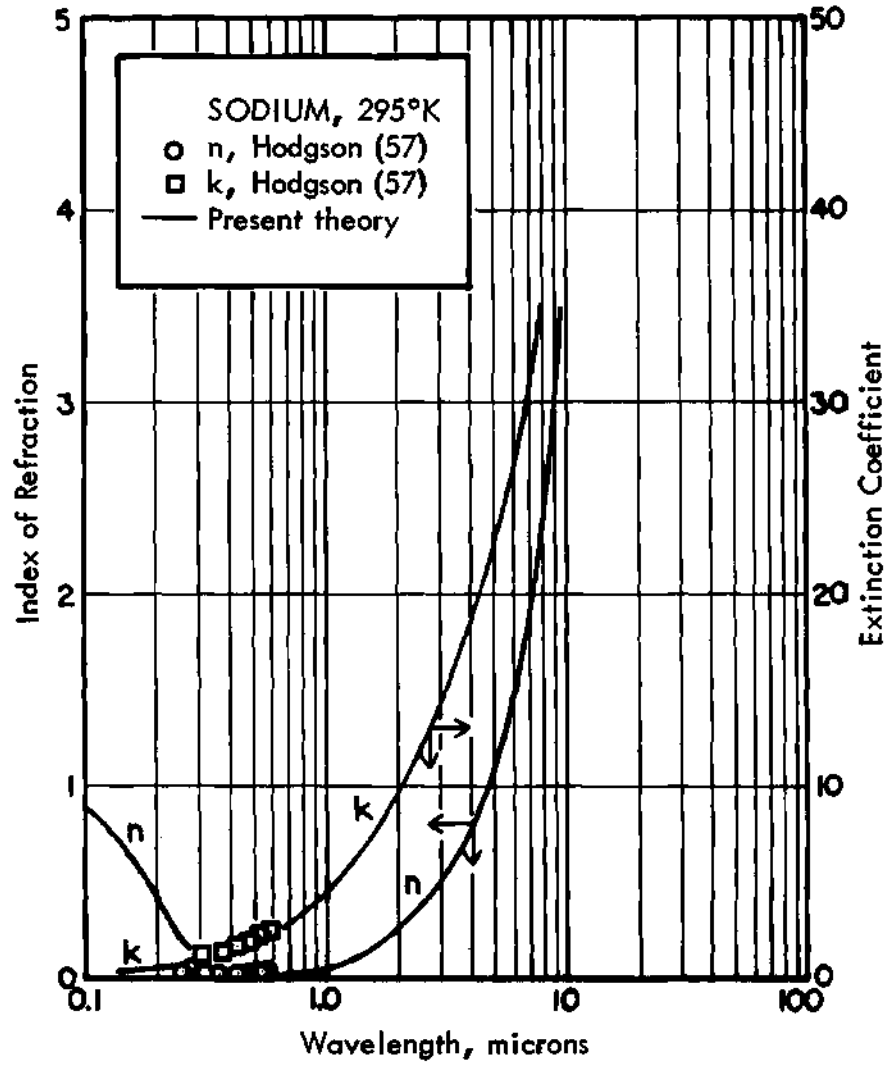


Figure 14. Optical Constants of Sodium at Room Temperature

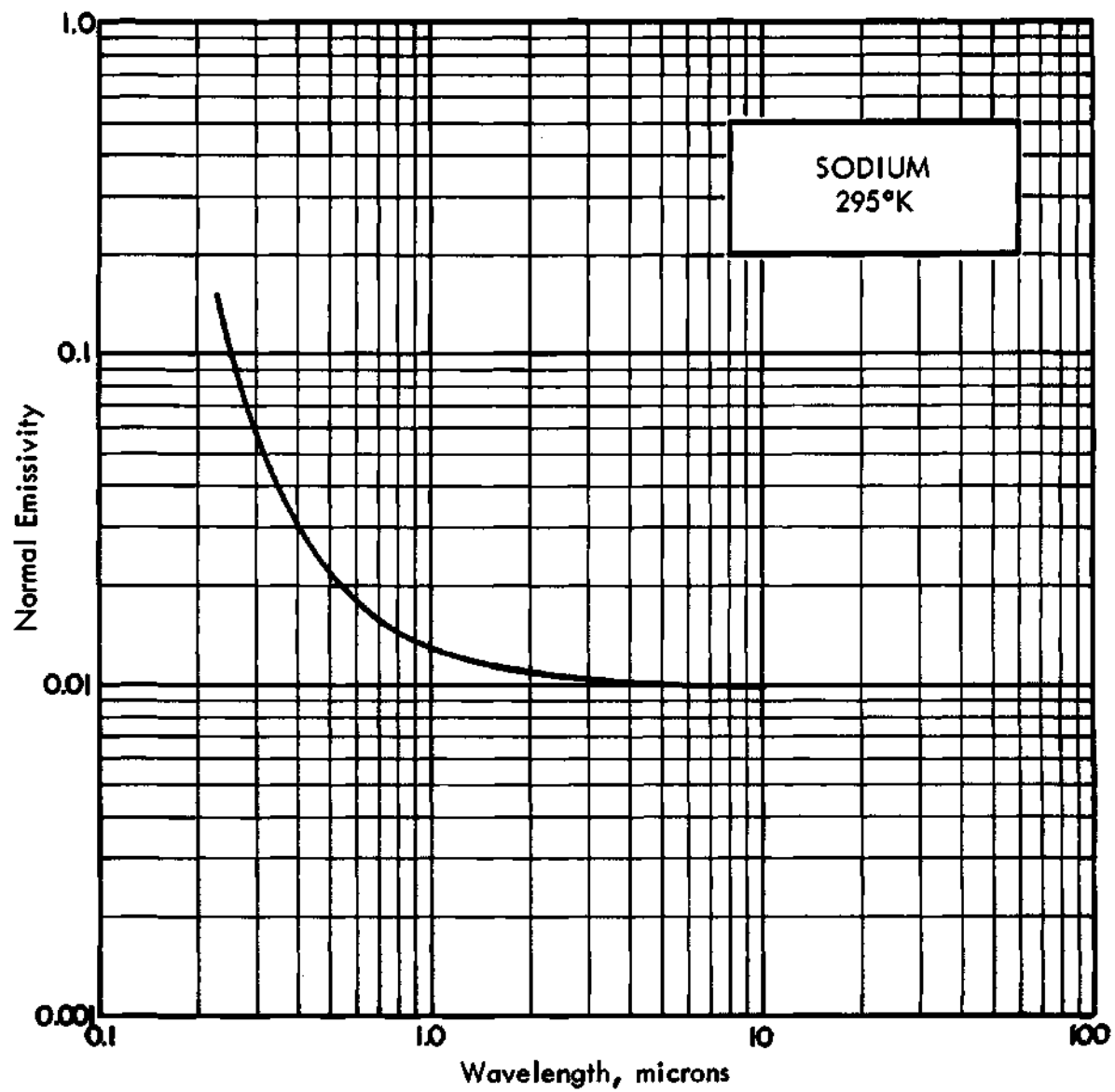


Figure 15. Predicted Monochromatic Emissivity of Sodium at Room Temperature

The Noble Metals

The noble metals have been the subject of more experimental and theoretical optical studies than any other group of metals. They form face-centered cubic (fcc) lattice structures and, at ordinary and high temperatures, are the best electrical conductors of all metals. The Fermi surfaces of the noble metals are known to contact the first Brillouin zone at the center of each hexagonal face. A review of the optical properties and band structure of the noble metals has been presented by Suffczynski (59).

The total electron damping coefficient, as well as its individual components, are shown in Figure 16 for silver at room temperature. At short wavelengths the electron-electron interaction term dominates whereas for wavelengths above about 3 microns the electron-phonon and impurity interaction terms become most important. As would be expected, the total damping coefficient approaches a constant value in the far infrared. The rapid increase of Γ_T as wavelength decreases below about one micron would indicate a region of strong absorption. This, of course, is observed experimentally and is usually attributed to interband transitions. In the present model it is a result of our formulation of the electron-electron interaction. This might indicate a close relationship between Gurzhi's expression for the electron-electron damping coefficient, Eq. (125), and interband transition phenomena. The theoretical curves of Figure 16 are compared with the experimental results of Beattie and

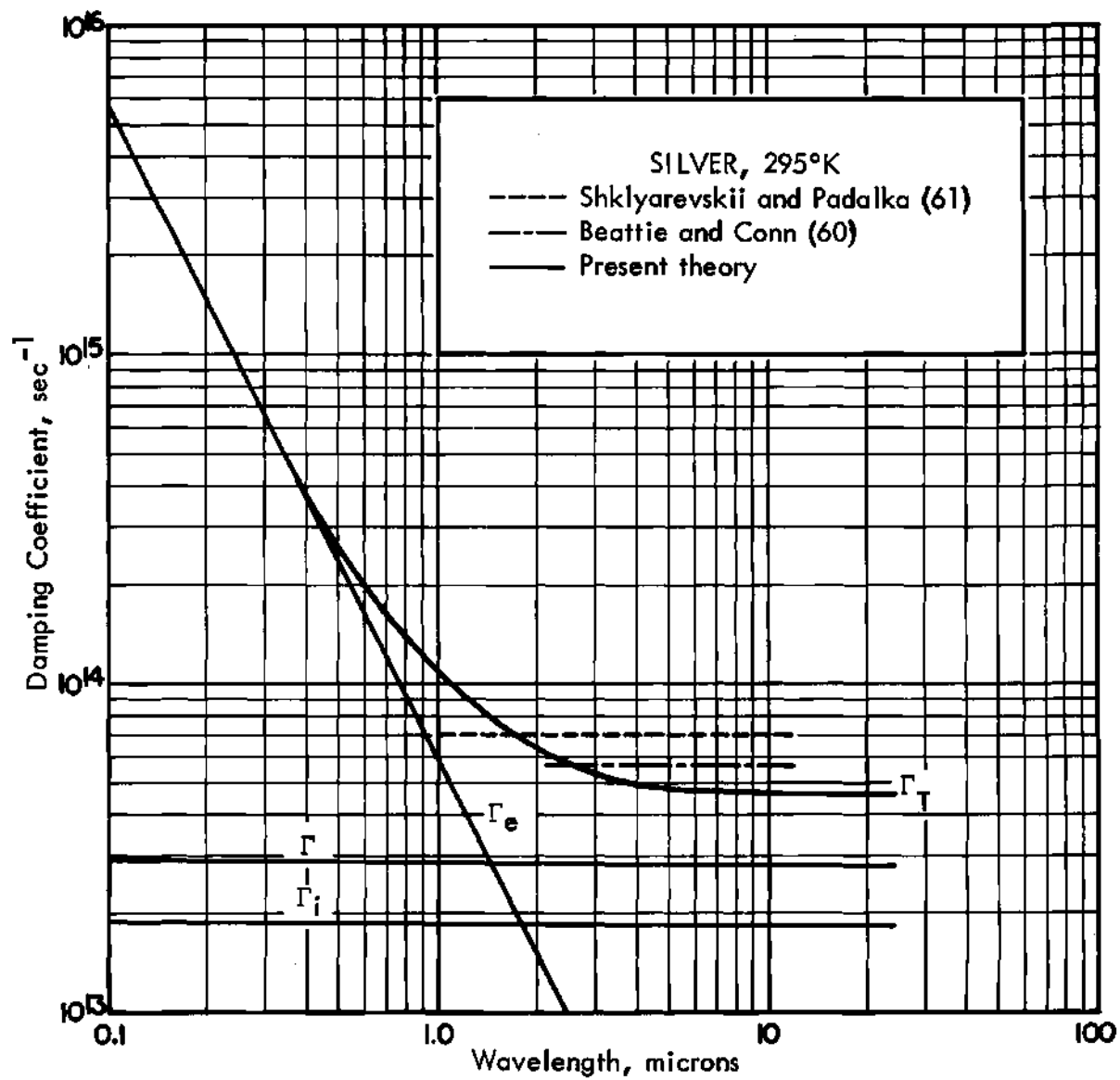


Figure 16. Electron Damping Coefficient of Silver at Room Temperature

Conn (60), who deduced a value of $\tau = 1/\Gamma_T$ from optical data over the wavelength range of 2 to 12 microns, and Shklyarevskii and Padalka (61), who used data from 1 to 12 microns. Hodgson (62) obtained a value very near that of Shklyarevskii and Padalka.

The theoretical nature of the damping coefficient at high temperatures is illustrated for silver at 1000°K in Figure 17. The electron-phonon interaction term has assumed even greater importance as would be expected because of the increased thermal activity of the lattice. However, the electron-electron term still dominates at short wavelengths. As temperature increases the damping coefficient increases and the region of strong absorption shifts to include longer wavelengths. One would expect, therefore, that absorptivity (or emissivity) would increase with temperature as is indeed the case. The values of C_e and Γ_i used to obtain the theoretical damping coefficient were those deduced from the experimental results of Padalka and Shklyarevskii (52) and given in Appendix I.

The values of the optical constants n and k predicted by the theory for silver at room temperature are compared with experimental data in Figures 18 and 19. Agreement is generally very good. The theory predicts slightly low in the case of the index of refraction and even less slightly high for the extinction coefficient at wavelengths above one micron.

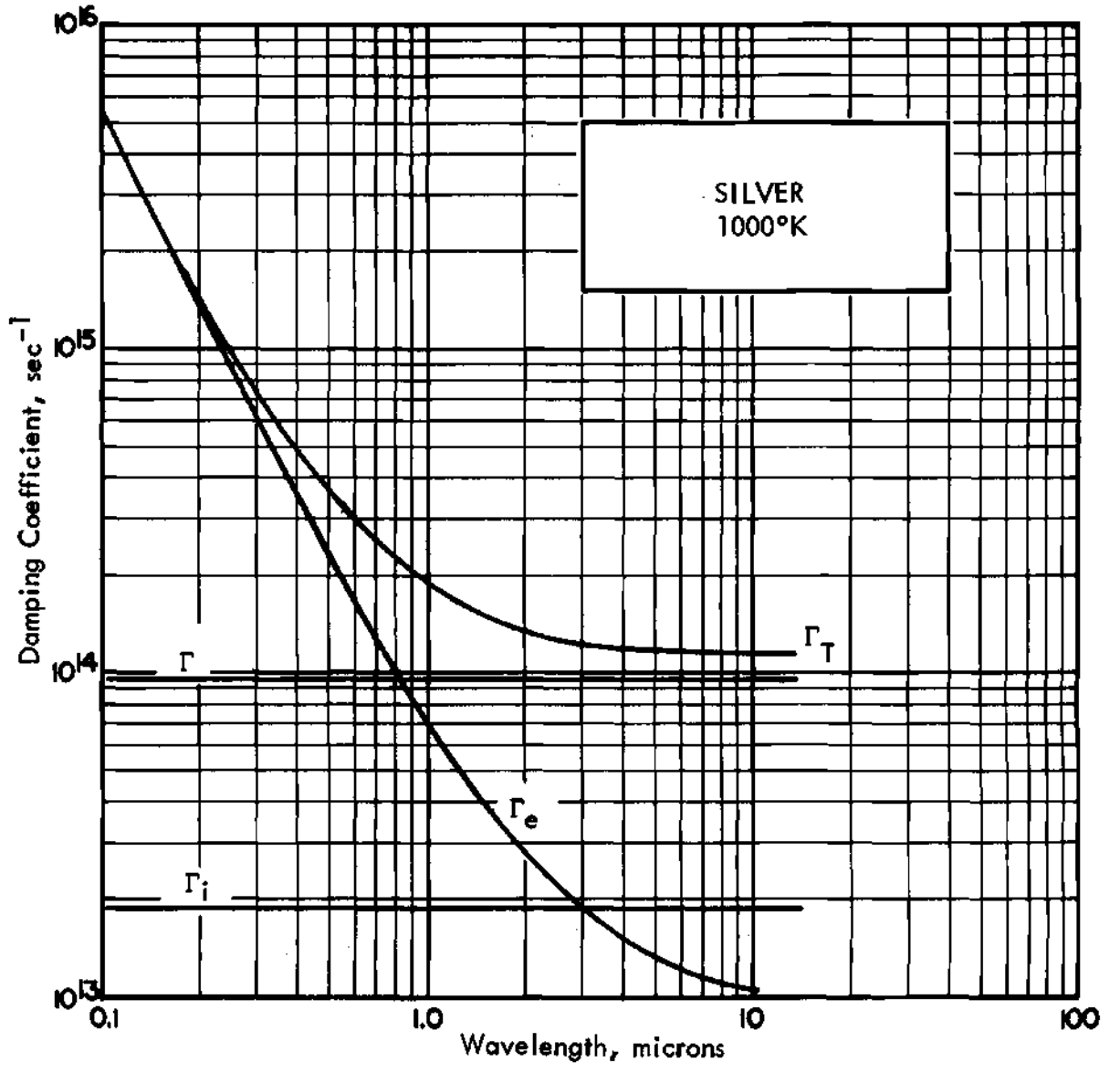


Figure 17. Predicted Electron Damping Coefficient of Silver at 1000°K

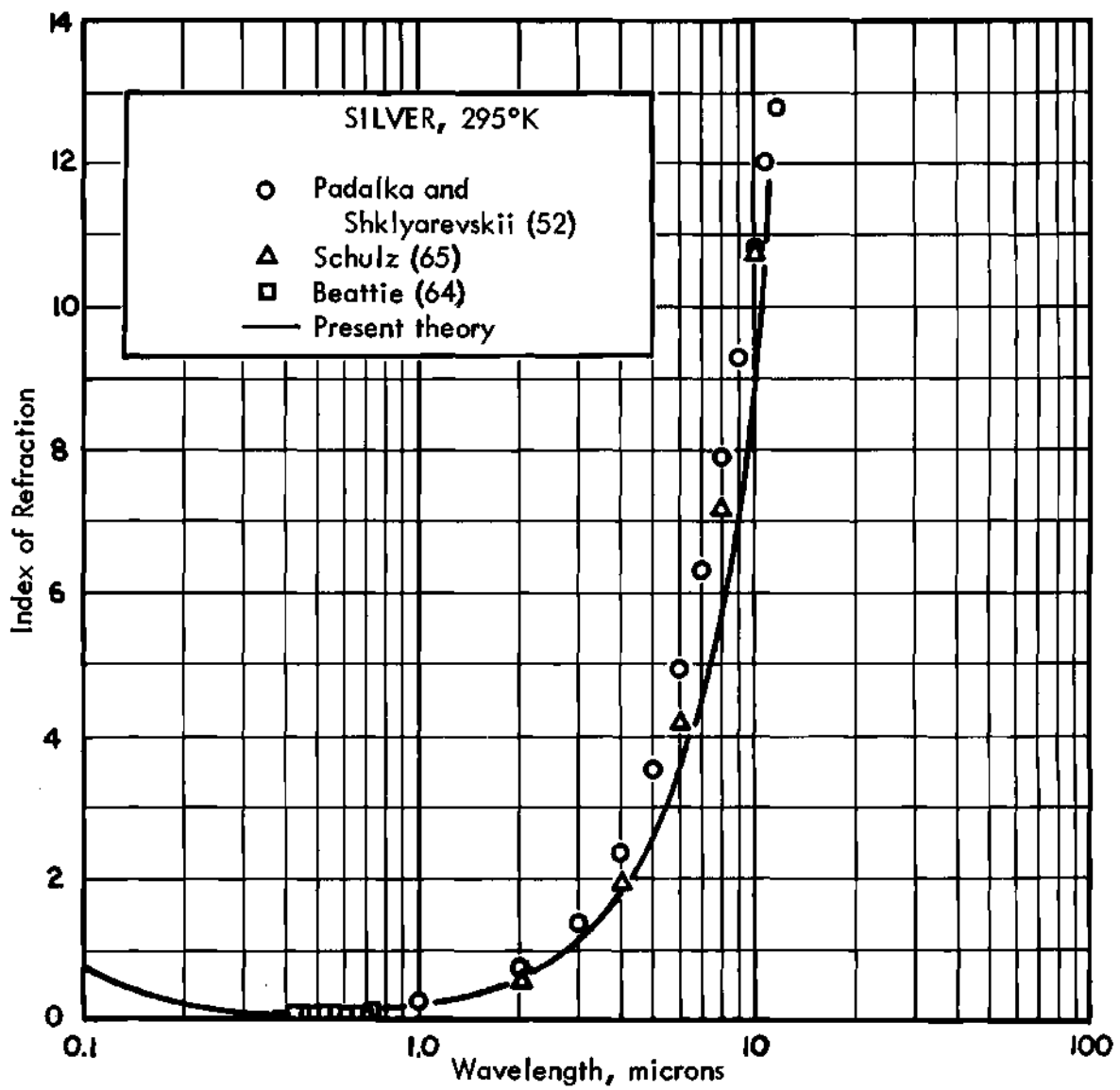


Figure 18. Index of Refraction of Silver at Room Temperature

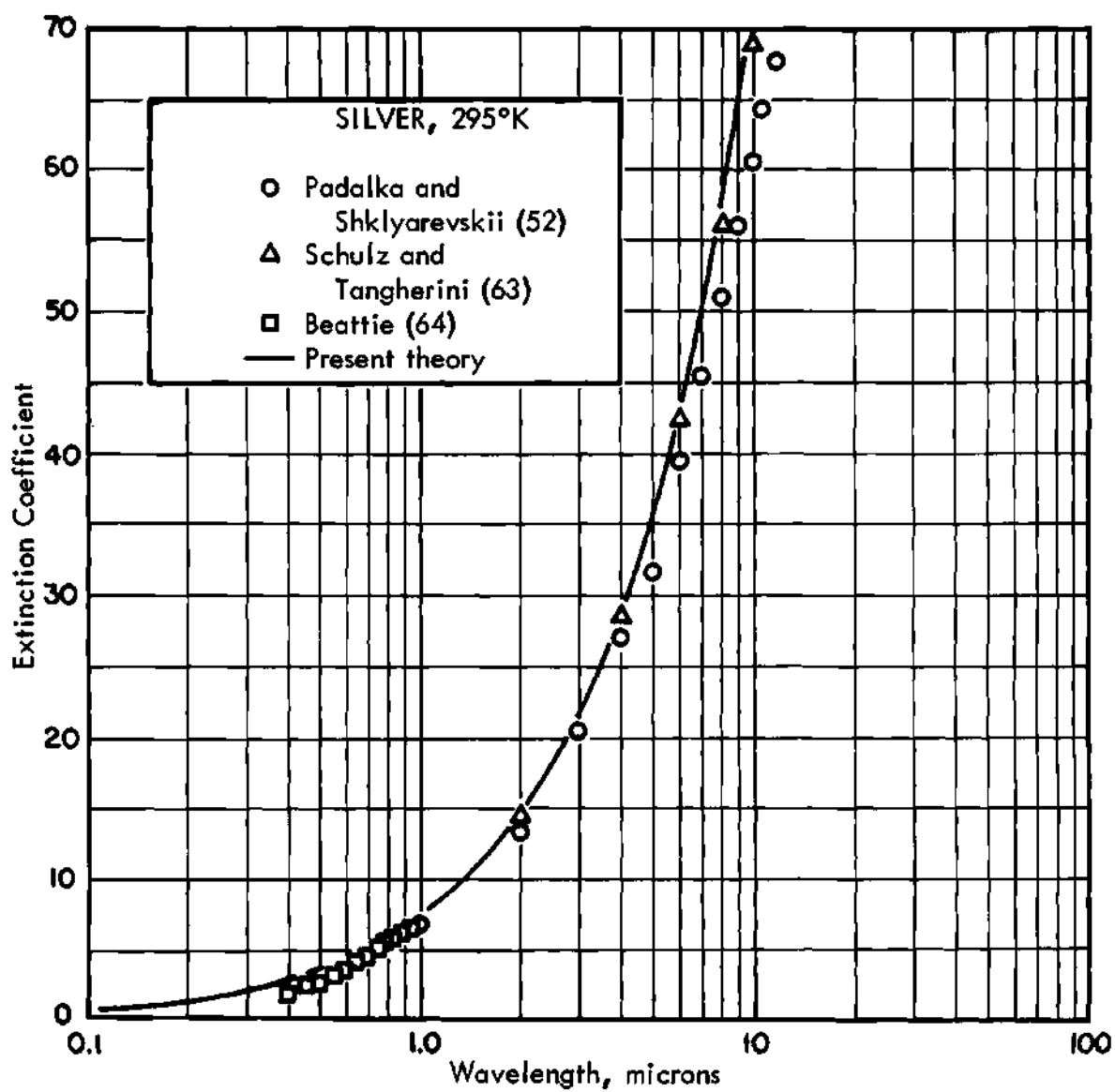


Figure 19. Extinction Coefficient of Silver at Room Temperature

The normal monochromatic emissivity of silver at room temperature is shown in Figure 20. Agreement between theoretical and experimental values is good although difficult to evaluate quantitatively because of the scatter of the measured data. Ehrenreich and Philipp (66) list the threshold for interband transitions in silver as 3.9 eV which corresponds to a wavelength of 0.32 microns. From Figure 20 it can be seen that this is very near the wavelength below which the theory predicts emissivity values smaller than the available experimental data. The variation of the emissivity of silver with temperature, as predicted by the theory, is shown in Figure 21.

The normal monochromatic emissivity of gold at room temperature is shown in Figure 22. The experimental values of C_e and Γ_1 obtained from the data of Padalka and Shklyarevskii (52) were used to compute the theoretical emissivity values. The theoretical curve lies below most of the experimental data. This was a general trend for the metals studied and will be discussed later in this chapter. The interband transition threshold for gold is at about 2.4 eV or 0.52 microns. The theory, however, predicts reasonable values of the emissivity for even shorter wavelengths. Figure 23 shows the temperature dependence of the normal monochromatic emissivity of gold. The only high-temperature data available are those of Maki and Plyler (70) for wavelengths between 4 and 13 microns.

Copper is of particular interest among the noble metals. It is lighter than silver or gold and, for this reason, has been the subject

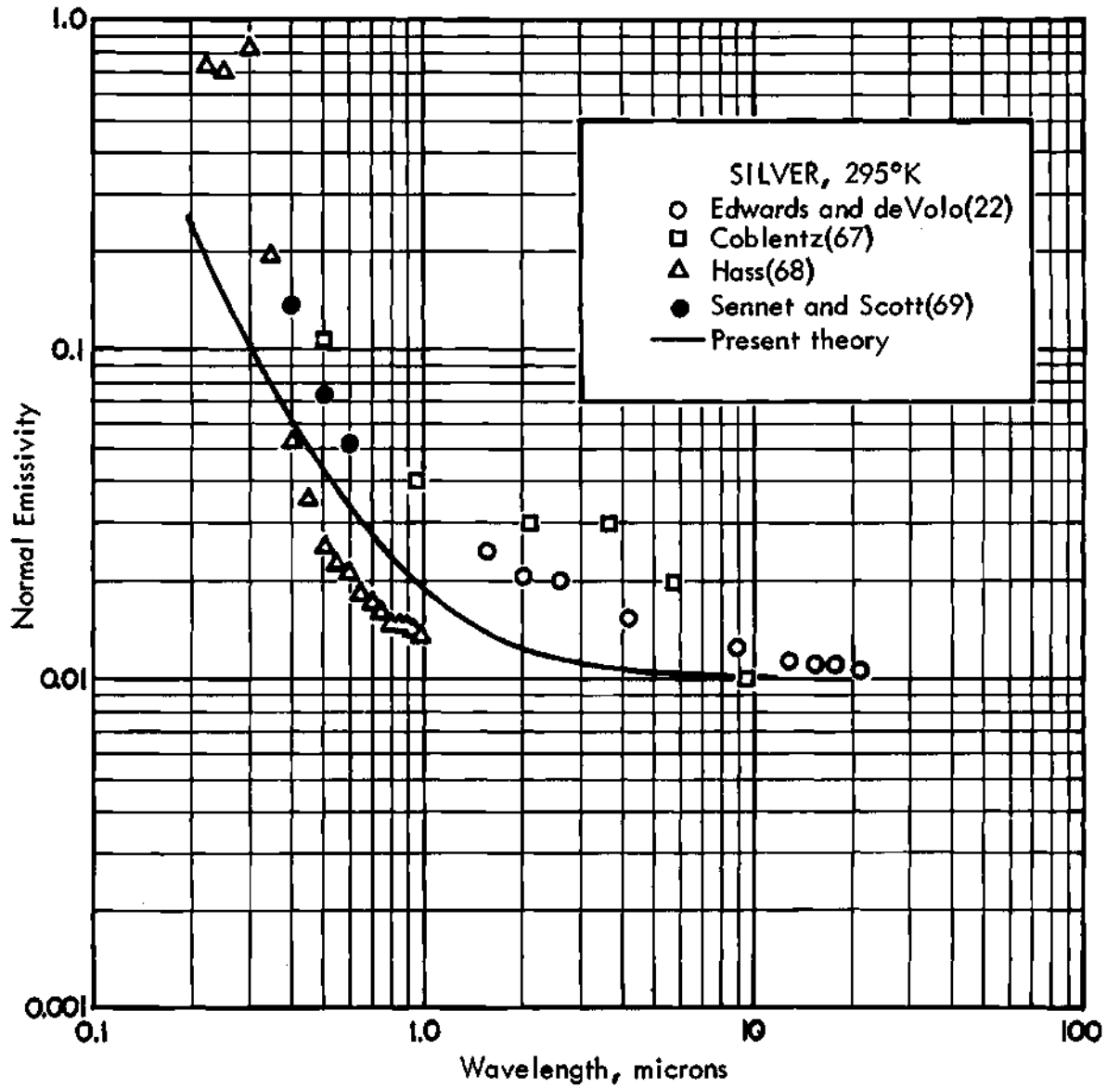


Figure 20. Monochromatic Emissivity of Silver at Room Temperature

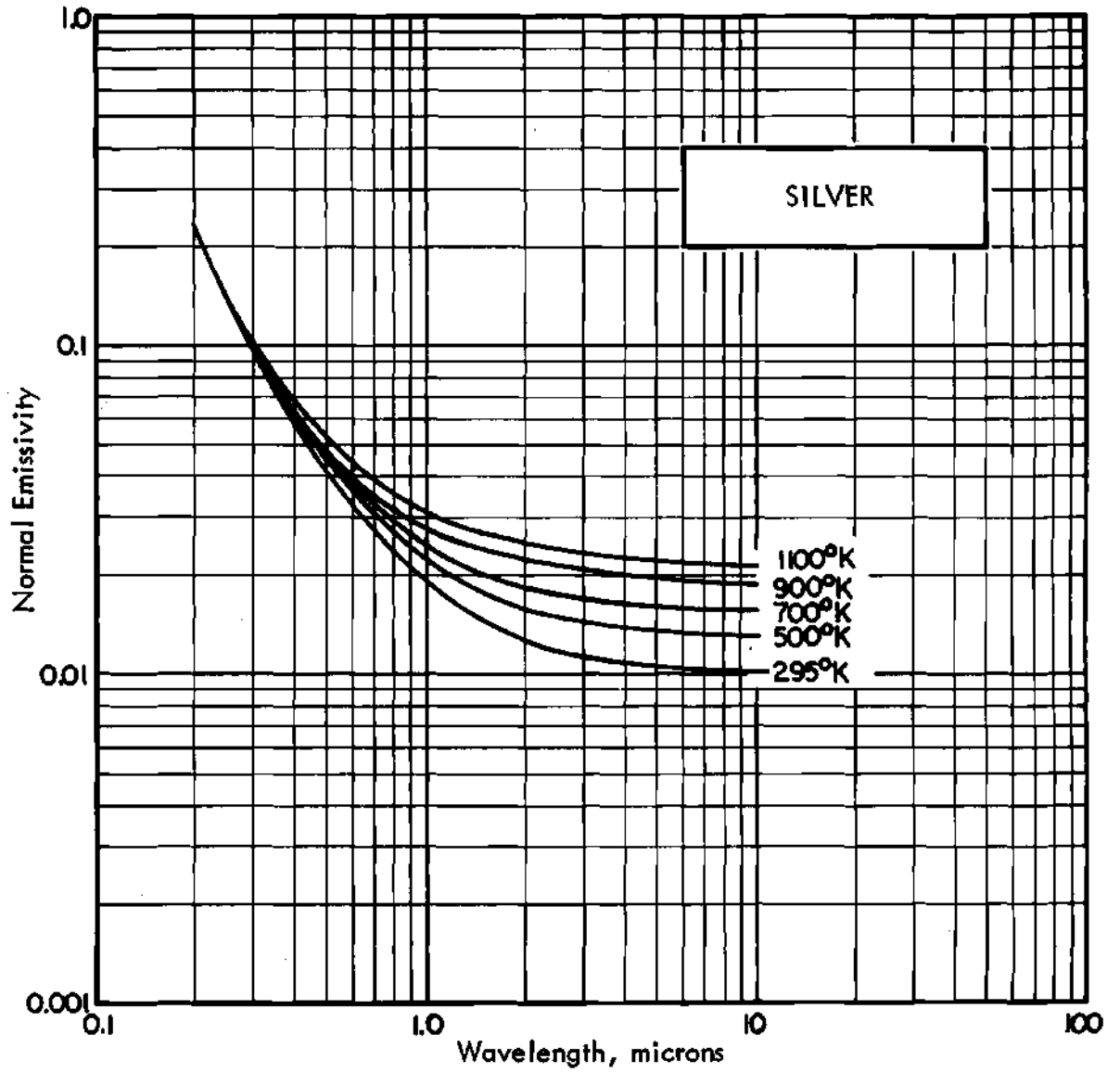


Figure 21. Predicted Monochromatic Emissivity of Silver as a Function of Temperature

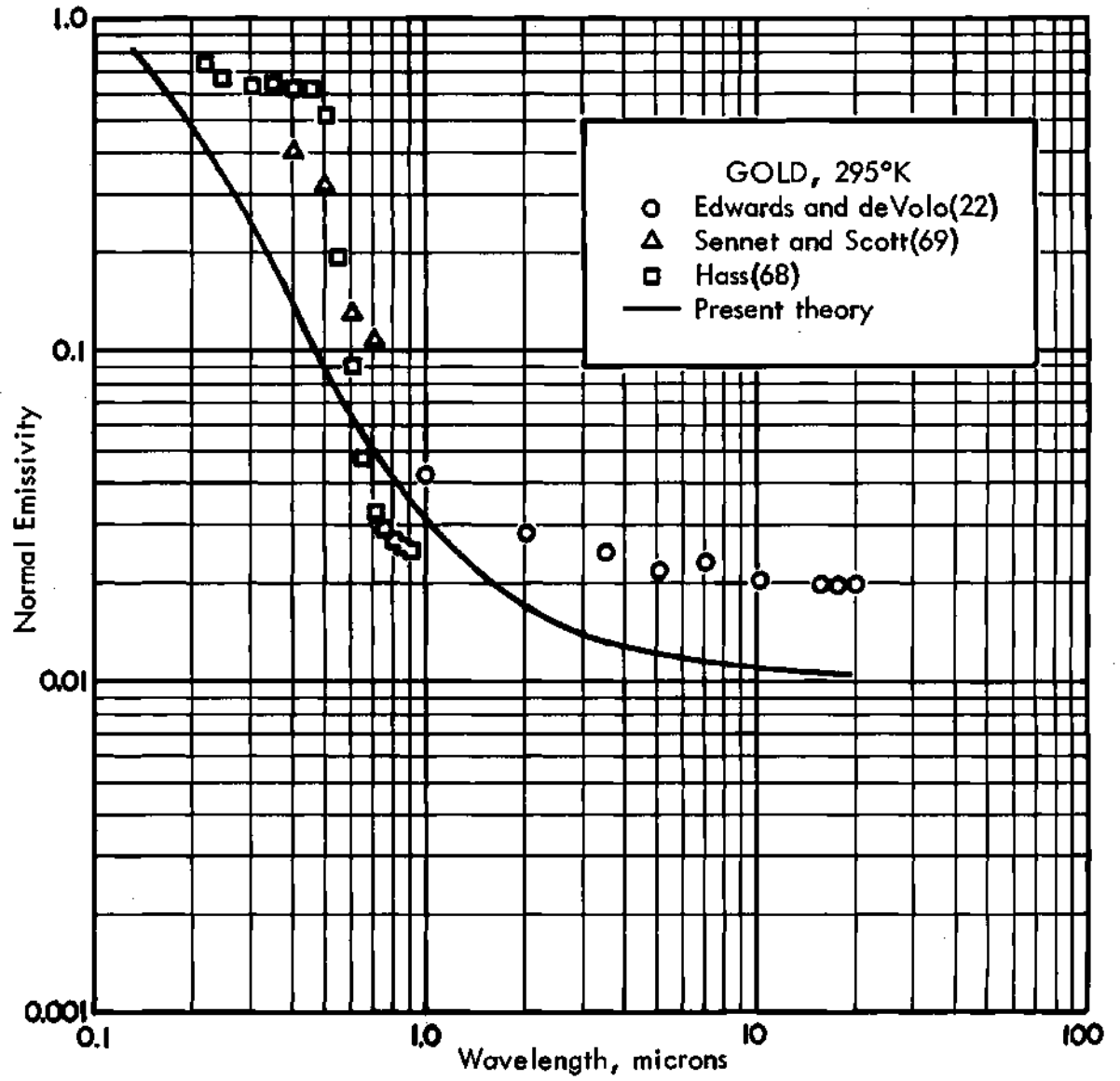


Figure 22. Monochromatic Emissivity of Gold at Room Temperature

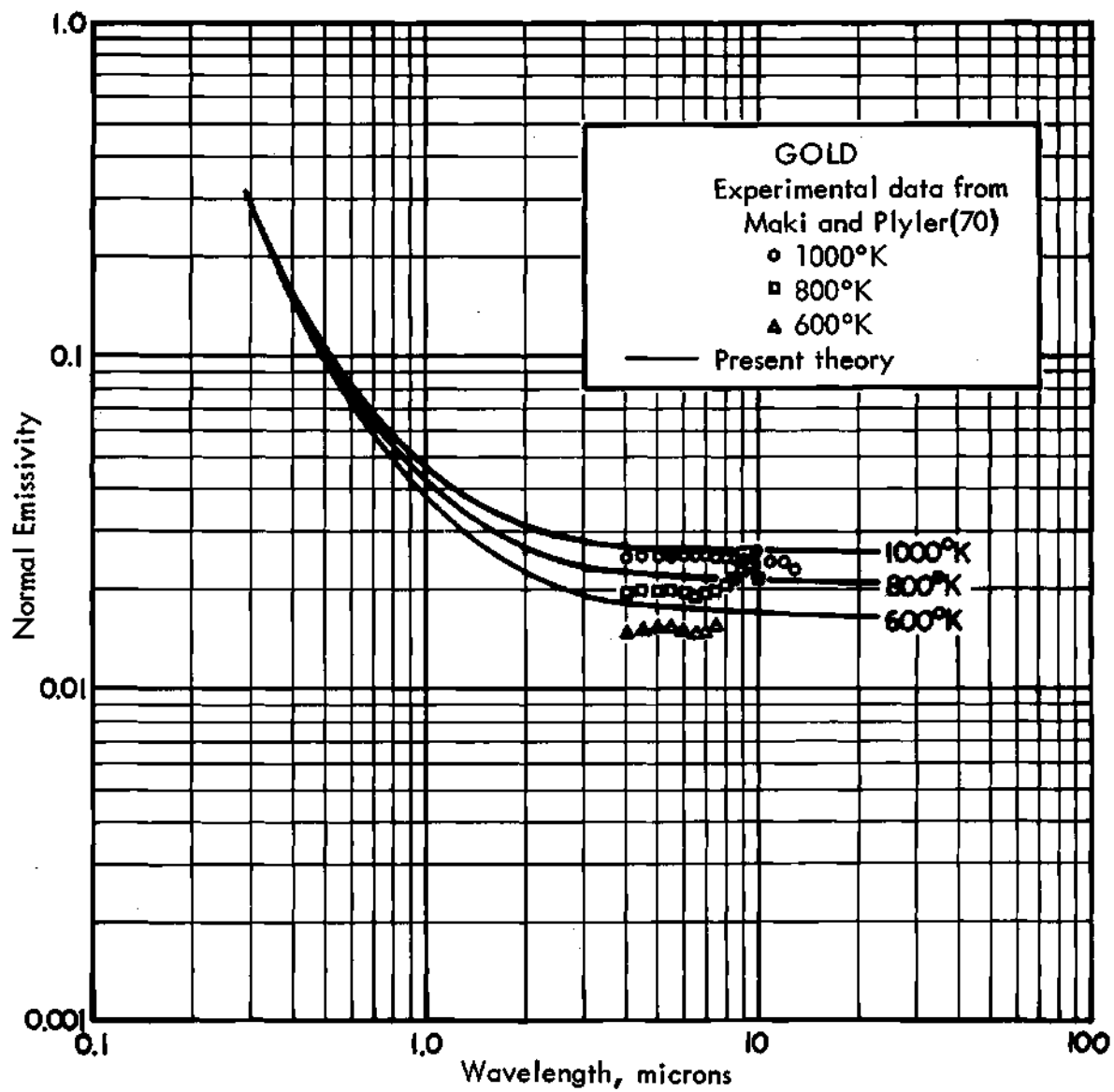


Figure 23. Monochromatic Emissivity of Gold as a Function of Temperature

of more band structure studies. Considerable experimental data are available concerning the electronic structure, optical properties and thermal radiation properties of copper at room temperature. Nonetheless, no data are available from which we can directly obtain the frequency- and temperature-independent constants C_e and Γ_i as was the case for silver and gold. Because their electronic structures are similar, we would expect that values of C_e and Γ_i for copper would be comparable with those of silver and gold. As shown in Appendix I, however, the values obtained from Eqs. (128) and (130) are appreciably smaller in both cases than the experimental results would indicate. We find that if we use the computed values in the calculation of the emissivity, the theoretical values are smaller than the available data in all portions of the spectrum.

The results of an investigation to determine the influence of the constants C_e and Γ_i on the theoretical values of the emissivity of copper are shown in Figure 24. The lower curve, numbered 1, was obtained using the values of C_e and Γ_i computed from Eqs. (128) and (130) and listed in Appendix I. The family of curves immediately above this, numbered 2 through 5, represent the same value of Γ_i but different values of C_e . The curves labeled A and B represent adjustments of both C_e and Γ_i . The effect of an independent increase in C_e can be seen to be a shift of the high absorption range to longer wavelengths; however, the long wavelength values remain unaffected. This is reasonable when

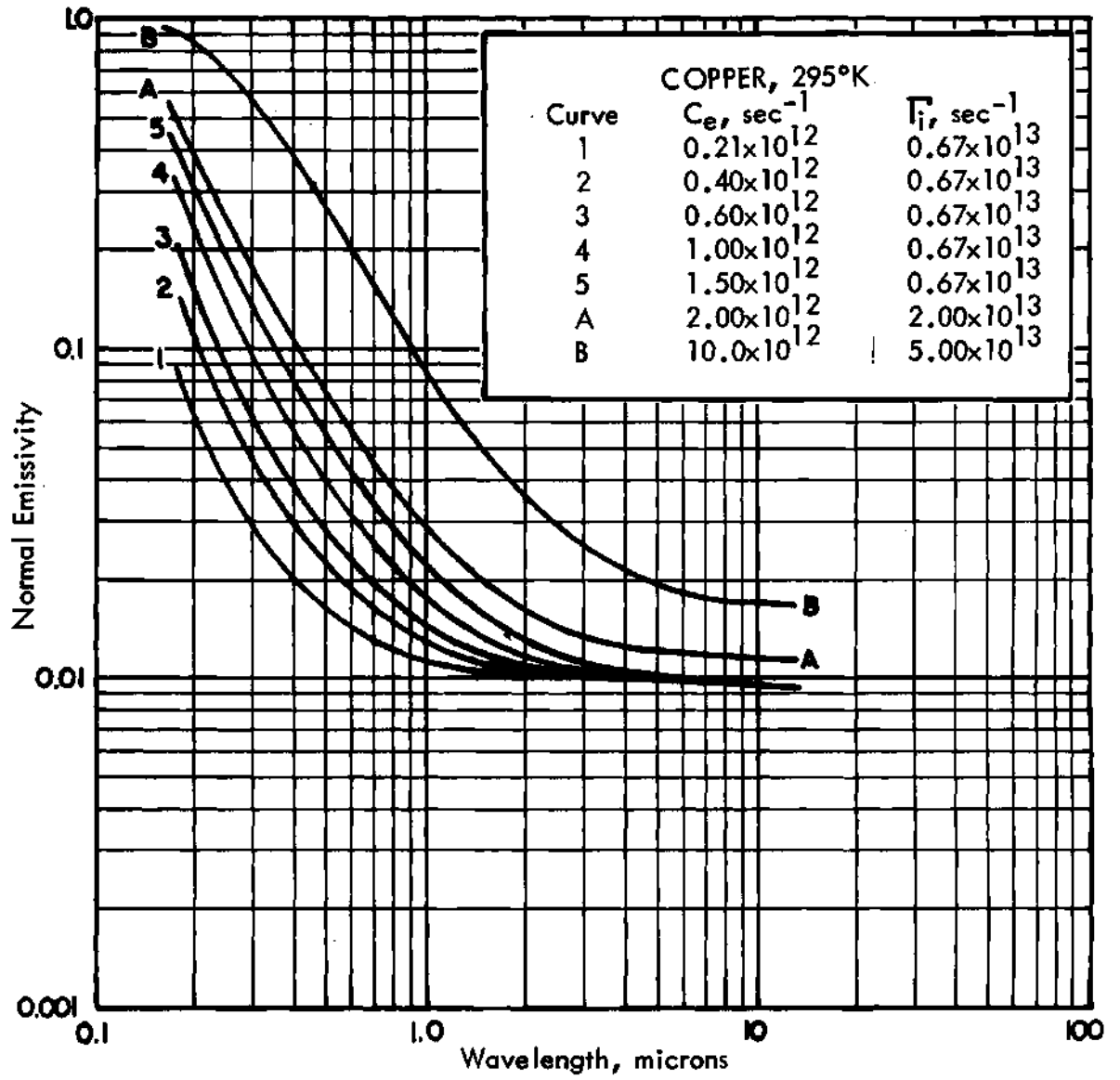


Figure 24. The Predicted Effect of C_e and Γ_i on the Monochromatic Emissivity of Copper at Room Temperature

one considers the influence of the electron-electron interaction model on the damping coefficient as shown for silver in Figure 16. When C_e is increased the electron-electron damping coefficient increases. At short wavelengths this results in an increase in absorption. However, at longer wavelengths where $\Gamma_e \ll \Gamma$ a change in C_e does not appreciably influence the total damping coefficient. Conversely, because of the relative magnitudes of the electron-phonon and impurity damping terms, an increase in Γ_i causes an increase in absorption except in that part of the spectrum where $\Gamma_e \gg \Gamma_i$.

It is reasonable to expect that, if the values of C_e and Γ_i obtained for silver and gold from the data of Padalka and Shklyarevskii (52) are reasonably accurate, then the corresponding values for copper (and other metals) should be greater than those computed from Eqs. (128) and (130). It is also interesting to compare the influence of Γ_i on the emissivity with the effect of surface roughness. An increase in surface roughness generally causes an increase in the infrared emissivity. This is related to the irregularities in the metal at the surface which might also be regarded as a source of stationary imperfections which contribute to Γ_i . The value of the impurity damping coefficient obtained from Eq. (130) represents a bulk metal parameter because it is based on the residual resistivity. It does not, therefore, include the subsurface imperfections created by surface irregularities or methods of specimen preparation. Such effects would tend to increase the value of Γ_i .

The normal monochromatic emissivity of copper at room temperature is plotted in Figure 25. The theoretical curve is for $C_e = 10^{13}$ sec.⁻¹ and $\Gamma_i = 5 \times 10^{13}$ sec.⁻¹. The threshold for interband transitions in copper is 2.1 ev or 0.59 microns. This is very near the point where the theoretical curve in Figure 25 falls below the experimental data although the theory also predicts reasonably accurate values of emissivity at shorter wavelengths. The variation of the emissivity of copper with temperature is shown in Figure 26.

Aluminum

The thermal radiation properties of aluminum are of interest because aluminum is important as an engineering structural material and finds considerable use in thermal radiation systems. Its electronic structure has been studied by Ehrenreich, Phillip and Segal (74) who found that the most significant structure in the dielectric constant occurs at about 1.5 ev (0.83 microns) and that no appreciable structure is observed at higher energies. The data presently available indicate that the general topology of the Fermi surface of aluminum closely approximates that of the free-electron sphere, perhaps even more so than some of the noble metals (39).

Figure 27 shows the normal monochromatic emissivity of aluminum at room temperature. Values of $C_e = 7.5 \times 10^{12}$ sec.⁻¹ and $\Gamma_i = 2 \times 10^{13}$ sec.⁻¹ were used to obtain the theoretical curve. The structure

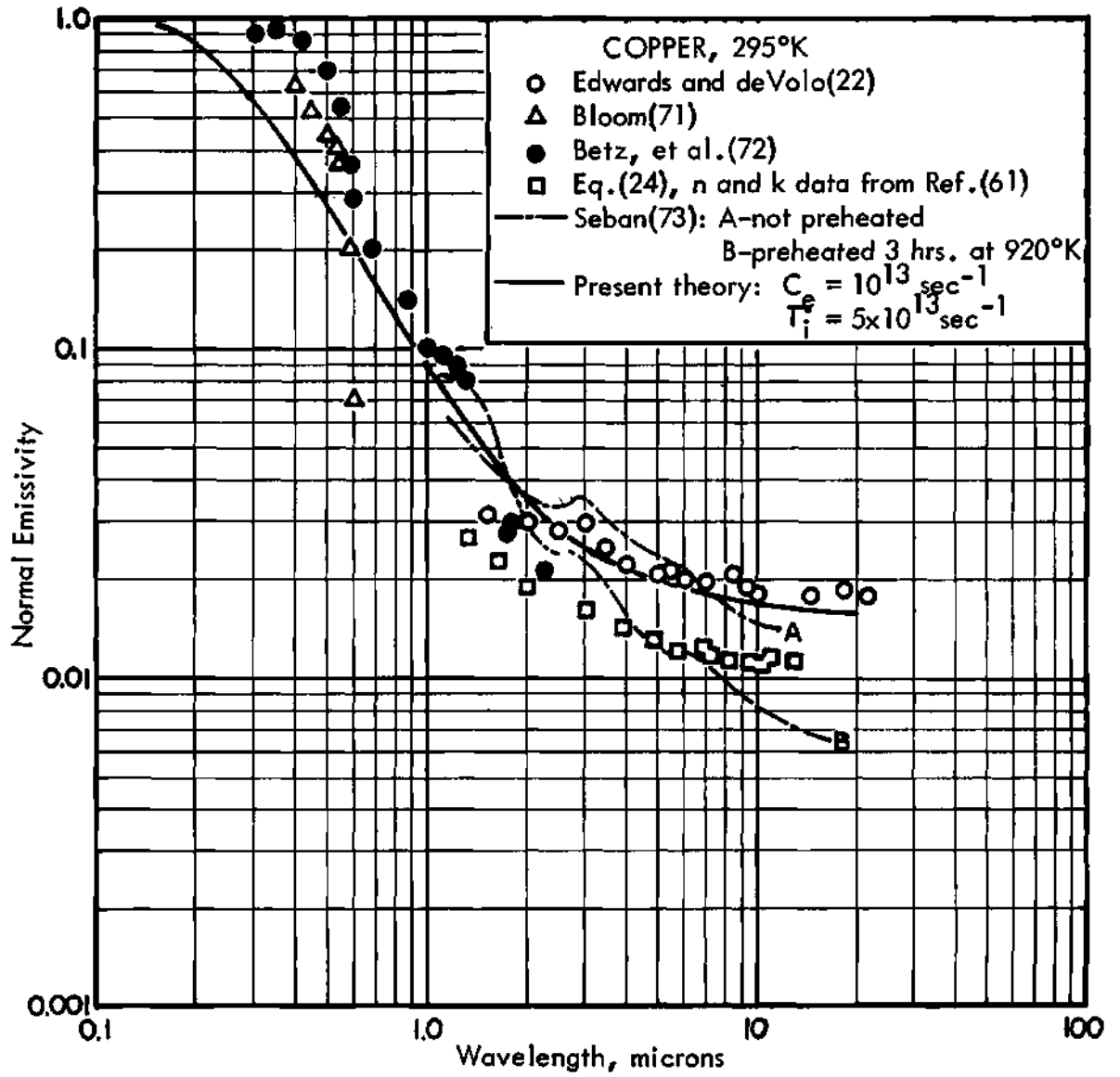


Figure 25. Monochromatic Emissivity of Copper at Room Temperature

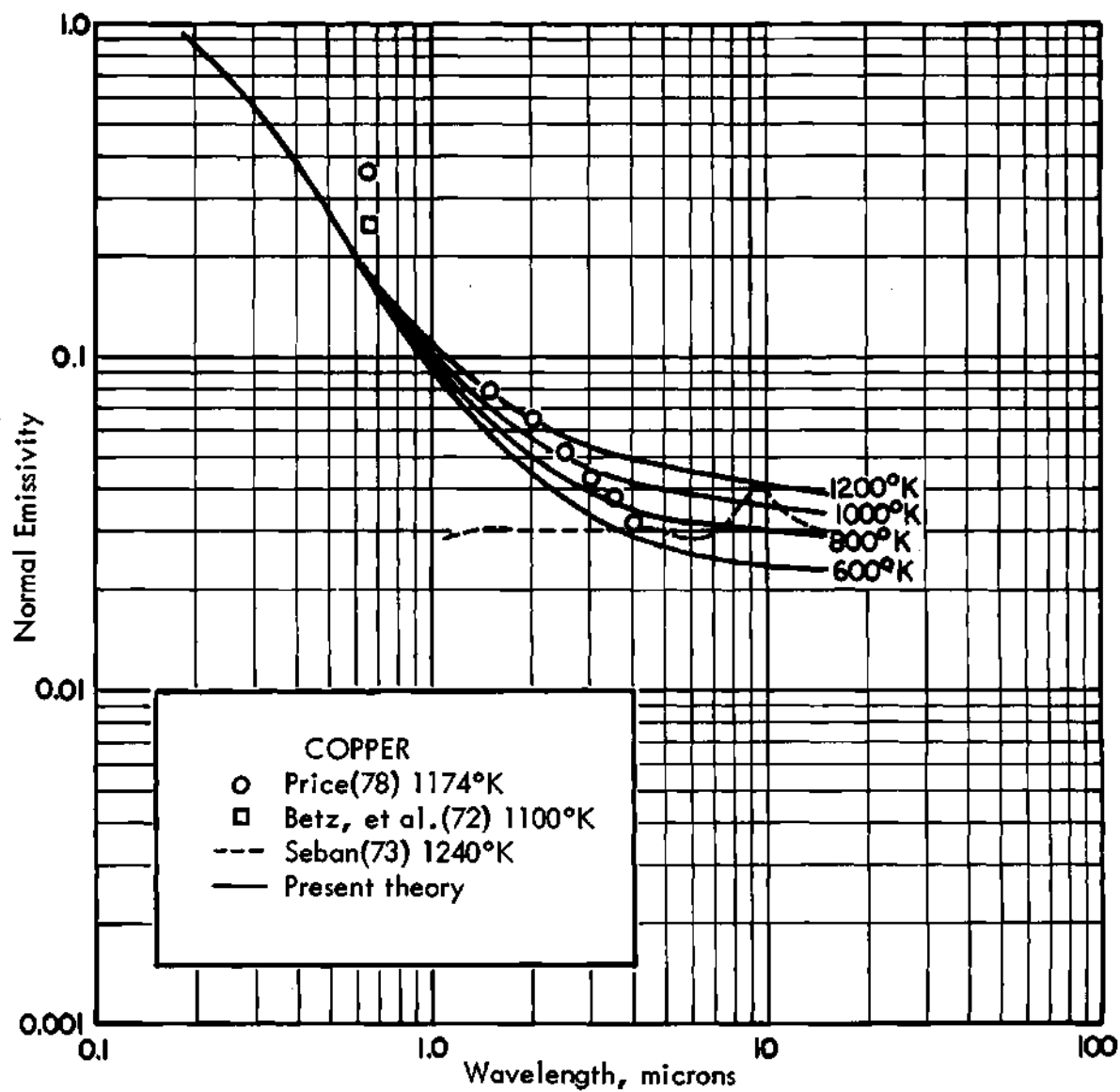


Figure 26. Monochromatic Emissivity of Copper as a Function of Temperature

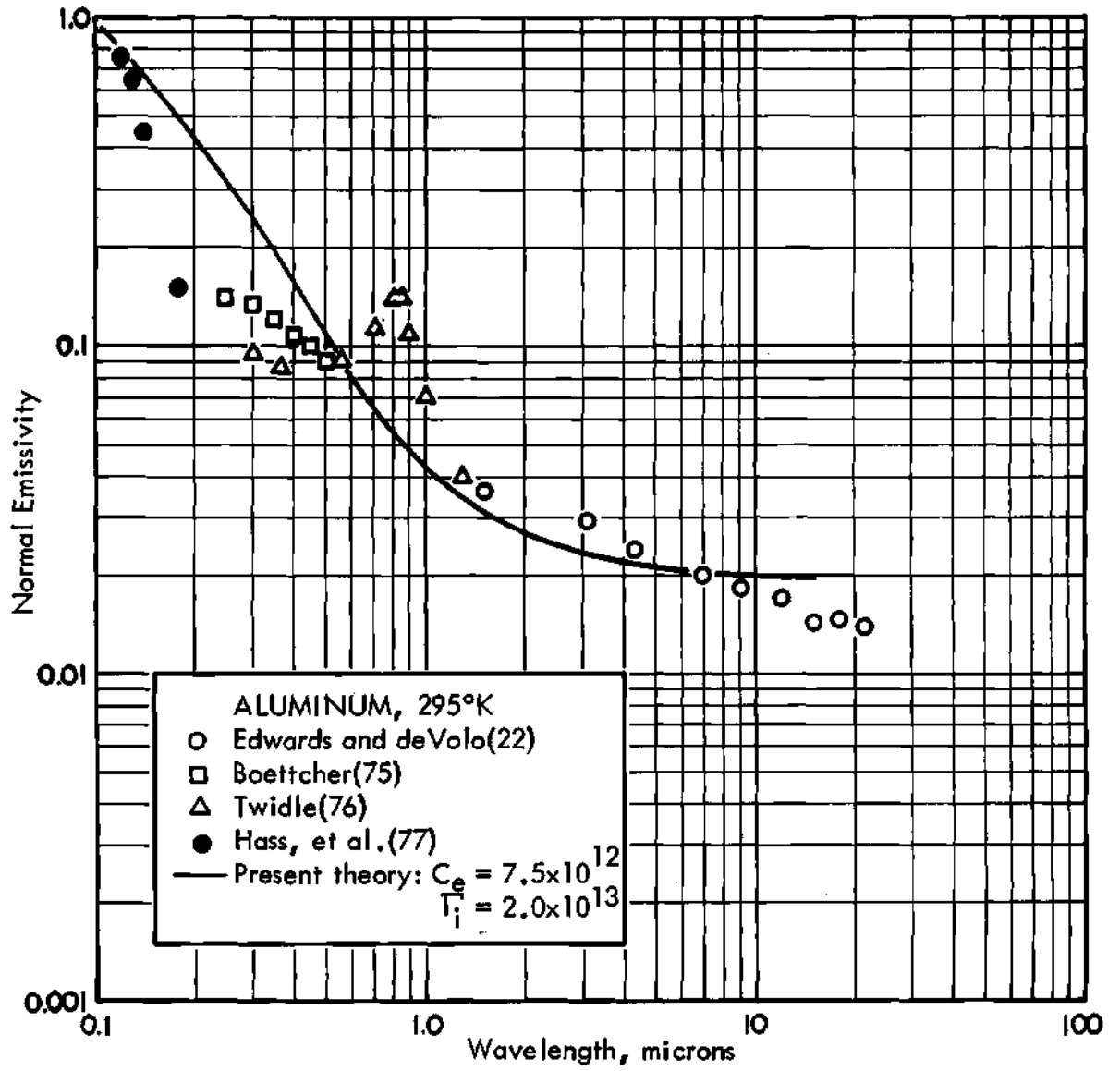


Figure 27. Monochromatic Emissivity of Aluminum at Room Temperature

observed in the dielectric constant at 1.5 eV due to interband transitions is also observed in the experimental emissivity data. The theory, of course, cannot duplicate the resulting region of high absorptivity which occurs over a relatively narrow wavelength band. The normal monochromatic emissivity of aluminum at different temperatures is shown in Figure 28.

Nickel

The transition metals are characterized by the fact that both d-band and s-band electrons can occupy states at the Fermi level. The resulting electronic structure is complex and band structure calculations are complicated. We would not expect, therefore, that the simple model employed in the present theory would provide very reliable correlation of thermal radiation property data for the transition metals. However, experiments show that the monochromatic emissivity of the transition metals differs from that of the noble metals, for example, by the fact that the region of high absorption begins at longer wavelengths. This same shift occurs in the computed values if the constant C_e is increased. Thus one might anticipate improved theoretical correlation in the case of the transition metals if sufficiently large values of C_e are used.

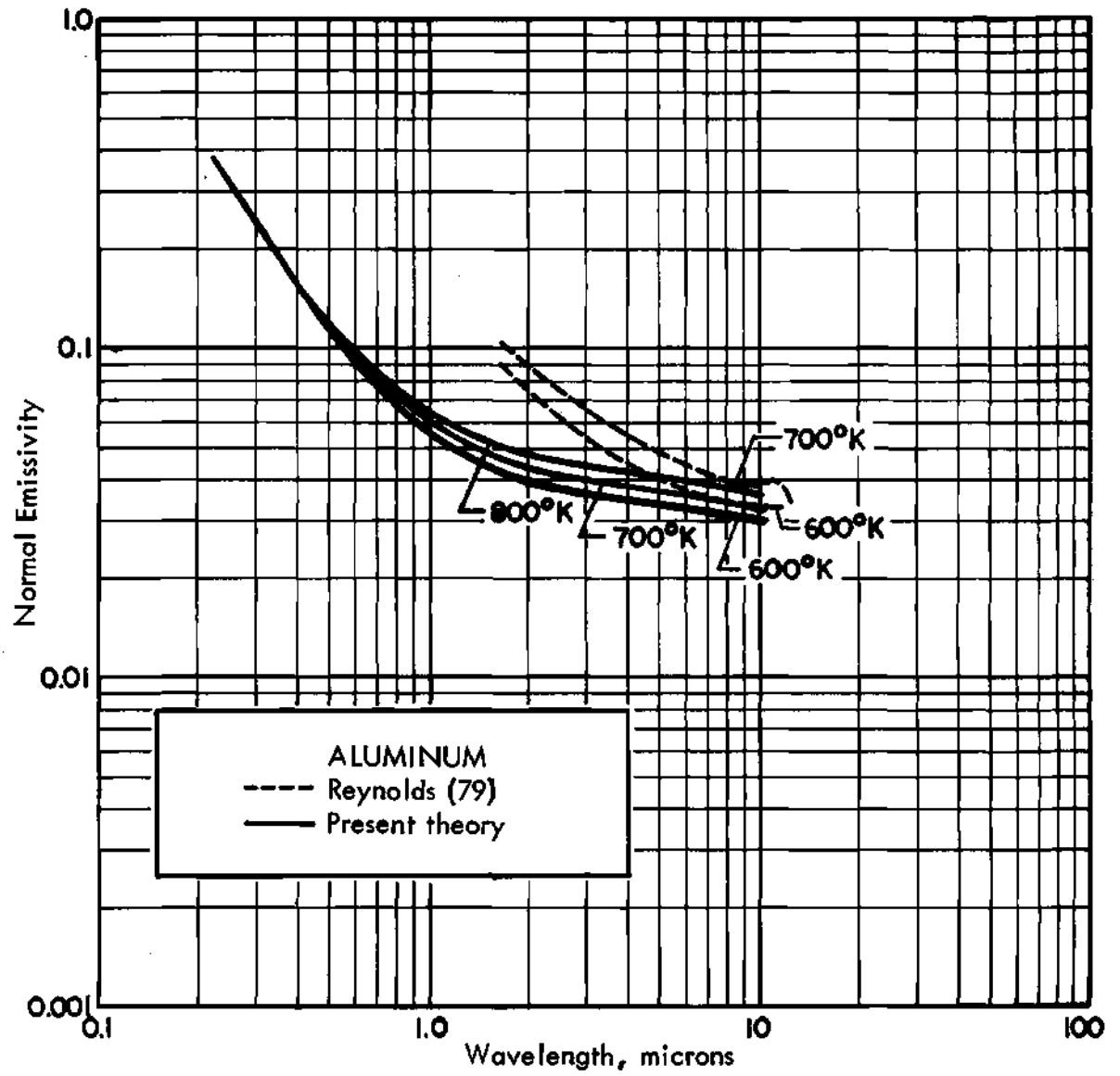


Figure 28. Monochromatic Emissivity of Aluminum as a Function of Temperature

The normal monochromatic emissivity of nickel at room temperature is plotted in Figure 29. Reasonably good correlation between experimental and theoretical values for wavelengths above about one micron is obtained for an electron-electron interaction constant of $C_e = 8 \times 10^{13}$ sec.⁻¹. This is somewhat higher than the values used for the monovalent and multivalent metals, as would be expected. The free-electron plasmon energy, 8.3 ev, was used in the theory and the electron velocity of the Fermi level was assumed to be that of the s-state electrons ($v_F/c = 0.0033$, see Appendix I). Ehrenreich, Phillip and Olechna (80) have observed structure in the dispersion of the dielectric constant at photon energies of 0.3 and 1.4 ev which corresponds to 4.1 and 0.9 microns, respectively. The low energy transition appears to coincide with the beginning of the region of high absorption. The second structure at 0.9 microns is also observed in the experimental emissivity data but, of course, is not predicted by the theory. This high energy structure appears in the case of the other transition metals also as is evident from the data of Edwards and DeVolo (22) for chromium, molybdenum, platinum, tungsten and vanadium.

The variation of the normal monochromatic emissivity of nickel with temperature is shown in Figure 30. The theoretical curve for 1400°K lies between the two sets of data obtained by Seban (23) (73).

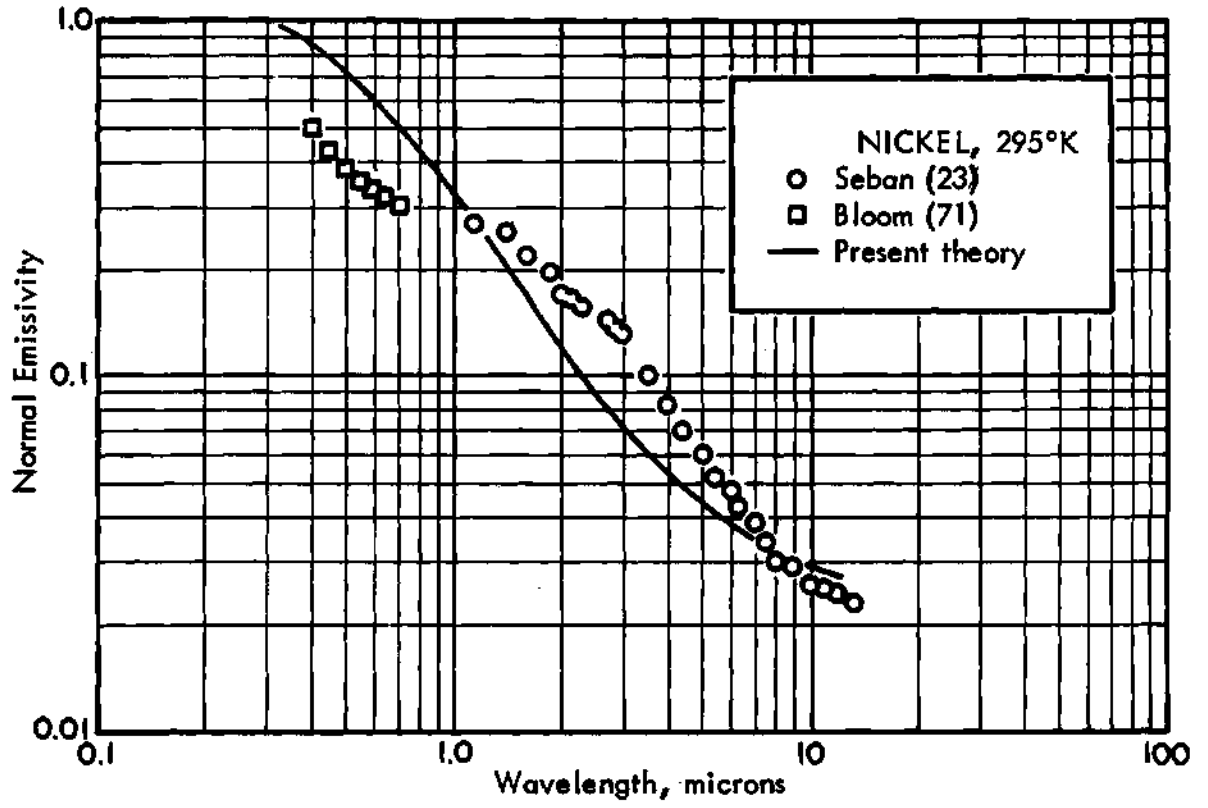


Figure 29. Monochromatic Emissivity of Nickel at Room Temperature

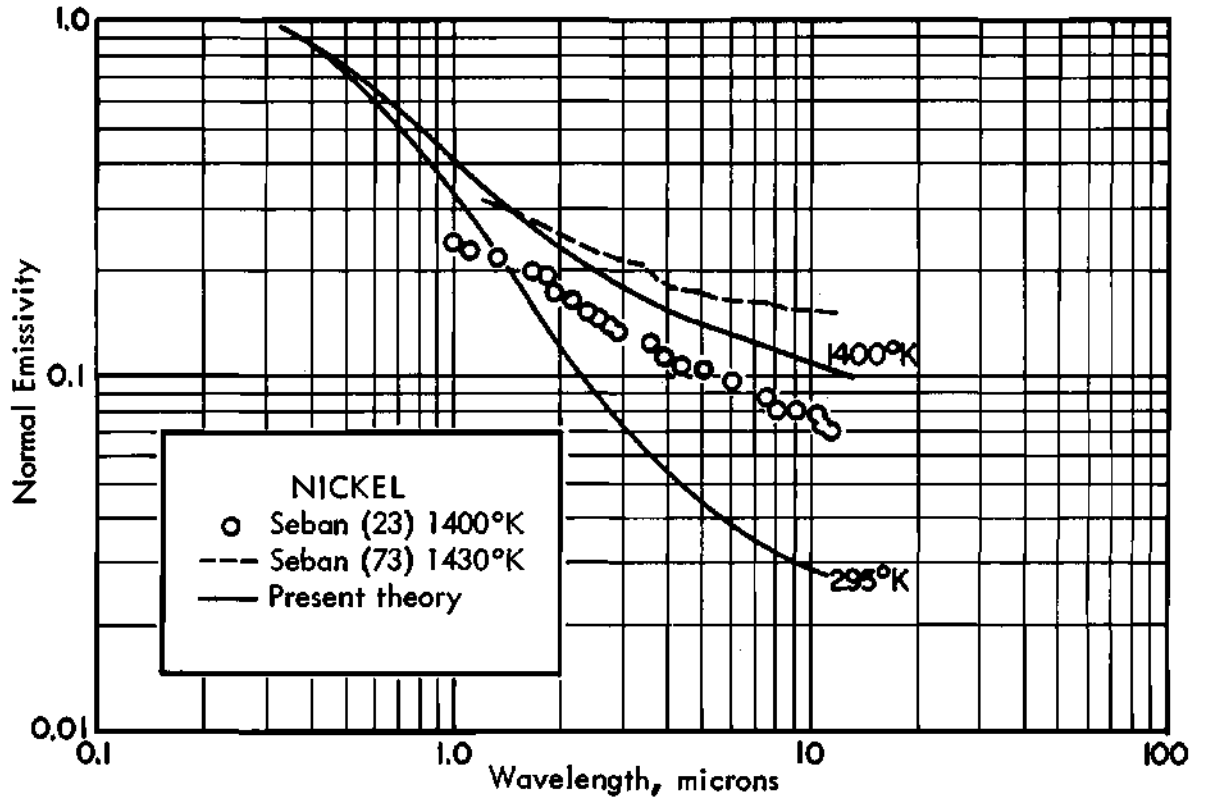


Figure 30. Monochromatic Emissivity of Nickel as a Function of Temperature

Discussion of the Theory

The analysis of the thermal radiation properties of metals presented in this thesis represents an attempt to utilize several concepts and analytical methods of solid state physics to formulate a theory which is useful in the engineering sciences. A limited number of investigations have been reported in the literature which were directed toward the study of quantum absorption phenomena in metals. Notable among these is the work of Gurzhi (81) (82) who derived a quantum-mechanical form of the Boltzmann transport equation for electrons in a metal subjected to an electromagnetic field. Gurzhi's analysis was concerned mainly with absorption at low temperatures but presents an example of an approach somewhat different from that used herein. Unfortunately, these studies, including the work of Gurzhi, do not yield relations which can be readily interpreted in an engineering sense. The present theory provides a number of interesting insights into the fundamental physical processes which give rise to the thermal radiation properties.

The principal analytical objective of the theory is to provide a means to compute the electron damping coefficient which serves as a quantitative measure of the ability of a metal to absorb thermal radiation. The radiation field expends energy by exciting the conduction electrons. But the electronic motion is damped by interaction with the other atomic constituents of the metal. The damping provides a mechanism by which

energy is transferred from the electrons to the lattice structure. Hence, the metal absorbs energy and its temperature rises. The conduction electrons also absorb energy from the lattice and emit energy into the radiation field. At thermal equilibrium these mechanisms are balanced and the metal maintains a constant temperature. For these reasons the damping coefficient is perhaps the most interesting parameter of the theory.

Experimental measurements show that as the wavelength of the monochromatic radiation field is decreased from the far infrared, the emissivity of a metal increases gradually until a wavelength region in the near infrared or visible part of the spectrum is reached at which the emissivity increases markedly to a value near unity in the near ultraviolet. This rapid increase in emissivity is attributed to the onset of quantum absorption. It can occur only when the photon energy is sufficient to induce quantum transitions between electronic states in the metal. According to the model used in the present theoretical development, the electron transitions are a result of simultaneous electron-photon and electron-phonon processes. A second-order perturbation analysis of such transitions yields a parametric grouping which can be interpreted as an electron-phonon damping coefficient. To this are added a term to account for the effects of interelectronic collisions and a constant term to account for the presence of impurities and stationary imperfections.

If the only mechanisms considered in the atomic model are the electron-photon and electron-phonon interactions, we find that the damping coefficient Γ is nearly independent of frequency as shown in Figure 11. However, it is influenced by temperature as would be expected from the fact that the phonon dispersion is a measure of the thermal energy of the lattice. The electron-phonon damping coefficient is the dominant damping term in the far infrared portion of the spectrum as shown for silver in Figure 16. Thus, in the far infrared, even if the electron-electron term is included in the model, the total electron damping coefficient is nearly frequency independent. This explains the utility of the simple Drude theory at long wavelengths. The Drude theory treats the damping coefficient as a phenomenological constant and relates it neither to frequency nor temperature. The empirical coefficients determined in the application of the Drude theory undoubtedly contain some contribution of impurity damping.

The relations developed in the present theory would be useful even if the model were restricted to the electron-phonon process and the application restricted to the far infrared because the theory gives the temperature-dependence of the electron-phonon damping coefficient. If Eq. (122) was used to determine the damping coefficient, the theory would provide a means of computing the monochromatic thermal radiation properties as a function of temperature at wavelengths above about 5 microns

for the monovalent metals. The inclusion of the electron-electron term extends the application of the theory to shorter wavelengths and to metals with more complex electronic structures.

The theory based on the electron-phonon interaction only is sufficient to predict the region of quantum absorption. However, even in the case of the monovalent metals, it appears necessary to include the electron-electron term in order to properly locate this region in the spectrum. If only the electron-phonon theory is used, the calculated emissivity values are less than experimental data although the shape of the curve is correct. The influence of the electron-electron interaction term is to shift the quantum absorption region to longer wavelengths. It thus becomes particularly influential in the correlation of the emissivity of the transition metals which is larger at longer wavelengths than that of the monovalent metals.

As was mentioned previously, the effect of the impurity damping term is appreciable only in the infrared where an increase in Γ_1 causes an increase in emissivity. It is interesting to relate this observation with the fact that an increase in surface roughness or a degradation of surface condition also causes an increase in emissivity. It is not unreasonable to interpret this as representing a relationship between what we have described as damping caused by stationary imperfections and what is regarded in experimental studies as a deviation from optically smooth surfaces. Perhaps if high purity specimens with extremely smooth

surfaces could be prepared, we would find that the experimental data would correlate more nearly with the values of Γ_i obtained from Eq. (130).

The theory provides a means of obtaining reasonably accurate calculated emissivity values at much shorter wavelengths than is possible with the Hagen-Rubens formula. Furthermore, it yields the temperature dependence which cannot be explained by the Drude theory. Correlation is possible even at wavelengths below the interband transition threshold. This can be attributed largely to the inclusion of the electron-electron term which is proportional to the square of the angular frequency. A discussion of the possible connections between interelectronic damping and interband transitions, however, is beyond the scope of this research.

Accurate correlation requires the selection of two temperature- and frequency-independent constants: the electron-electron collision constant and the impurity damping coefficient. Although these constants have some basis in the physical model, the most satisfactory results are obtained if they are determined by matching the theory to an experimental point. Even so, this represents a considerable improvement over the Drude-Roberts theory which requires the empirical determination of many arbitrary constants at each temperature. Furthermore, the constants in the present theory can be traced to their role in the electron interactions whereas the Drude-Roberts constants have no relation to an atomic

model. Once C_e and Γ_i have been determined at a specific frequency and temperature the values are applicable at all other frequencies and temperatures for which the theory is valid.

The temperature dependency of the emissivity is correctly predicted by the theory although it is difficult to assess the accuracy of the calculated values at high temperatures because of the lack of precise high-temperature emittance measurements. The theory correctly indicates that the temperature coefficient of emissivity is positive in the far infrared and decreases to near zero at some point in the visible or near infrared depending on the particular metal. However, the transition to very small negative temperature coefficients at even shorter wavelengths, which is observed with some metals, (the x-point) is not theoretically predicted. This would indicate that the x-point is the result of some phenomena not included in the atomic model; for example, the effects of bound electrons which are excited in the ultraviolet.

The quantum absorption region observed in the experimental emittance data of the monovalent metals and predicted by the theory coincides with the interband transition threshold which is determined by measurement of the dielectric constant. In the case of the multivalent and transition metals, the experimental data exhibit more dispersion structure but can also be correlated with the multiple interband thresholds. Therefore, if precise emittance measurements are coupled with the information provided by the theory, it should be possible to study

many of the microcharacteristics of metals. For example, if the theory is fitted to normal monochromatic emittance data, the various components of the total electron damping coefficient can be determined.

The wavelength region in which the theory appears to be valid for the metals studied includes the near infrared and, in some cases, part of the visible region as well as the far infrared. In the case of copper, for example, good agreement between experimental and theoretical emissivity values is obtained for wavelengths as short as 0.6 microns. For a copper surface at a temperature near the melting point (1356°K), the radiant power emitted in the wavelength region above 0.6 microns is more than 99.99 per cent of the total radiant power emitted by the surface. On the other hand, the same surface at the same temperature emits only 14 per cent of its total radiant power at wavelengths above 6 microns, the generally-accepted lower limit of the Hagen-Rubens formula. Thus, the theory provides analytical access to a wavelength region which is of considerable importance to thermal radiation analysis but which is outside the region of applicability of the simple classical theory.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Engineering studies of the thermal radiation properties of solids have rarely given more than passing reference to the basic fact that absorption and emission are quantum phenomena. The engineer is usually satisfied with experimental data and phenomenological investigations. Hopefully, the research described in this thesis indicates that useful and interesting results can be obtained by the application of elementary quantum concepts to the theoretical study of the thermal radiation properties of metals.

The following conclusions result from the study reported herein:

1. The theoretical relations which result from an analysis of the second-order processes involving electron-photon and electron-phonon interactions predict the existence of the experimentally-observed region of quantum absorption in metals.

2. The electron-electron interaction, as expressed by Gurzhi's relation, is important as an absorption mechanism in the visible and near infrared parts of the spectrum for metals at room temperature and above.

3. The impurity interaction can be treated as a constant addition to the total electron damping coefficient and can be important at

long wavelengths and moderate temperatures. At high temperatures its influence is diminished by the increased significance of the electron-phonon interaction.

4. The location of the region of quantum absorption in the spectrum is influenced by the value of a temperature- and frequency-independent constant, C_e , associated with the electron-electron interaction. The value of this constant increases with the complexity of the electronic structure of the metal.

5. The region of quantum absorption predicted by the theory occurs at frequencies which correspond with the threshold for interband transitions. This suggests a possible connection between the model used for electron-electron processes and interband transition phenomena.

6. With the proper selection of two constants, the theory can be used to correlate the normal monochromatic emissivity of not only the noble metals but also the transition metals, although not all details of the latter are predicted.

7. The theory suggests that the following mechanisms account for the absorption phenomena observed in metals at various parts of the spectrum: At short wavelengths the electron-electron interaction is the dominant absorption mechanism. This is the indication even at high temperatures, although the importance of the electron-phonon process increases as the temperature increases. The wavelength below which the

electron-electron process is dominant depends on the particular metal but usually lies in the visible or near infrared. At longer wavelengths the electron-phonon mechanism is dominant and is nearly independent of frequency, which explains the fact that application of the Drude free-electron theory is limited to the far infrared. The impurity interaction contributes to absorption in the far infrared but is usually appreciably less important than the electron-phonon process.

8. The relations which result from the theory provide an explicit formulation for both the frequency and temperature dependence of the normal emissivity. Neither the classical Drude theory nor the empirical Drude-Roberts theory provide the temperature dependence.

9. The theory significantly extends the wavelength range over which theoretical emissivity values can be obtained. The Hagen-Rubens formula is accurate only for wavelengths greater than about six-to-ten microns whereas the present theory provides adequate correlation at wavelengths in the visible spectrum for some metals. This extended range encompasses a part of the spectrum which is very important in high-temperature thermal radiation analysis.

10. The theory does not predict the short-wavelength x-point observed in the case of some transition metals. This suggests that the x-point is a result of some phenomena not included in the theoretical model, perhaps the high-frequency excitation of core electrons. The

theory does, however, indicate that the temperature coefficient of emissivity becomes vanishingly small as the wavelength is decreased.

11. The theory is sufficiently simple that it could be easily used in the routine correlation of emissivity data. An analysis of experimental thermal radiation property data within the framework of the theory indicates that the data reveal many features usually studied only in more sophisticated investigations of optical properties.

The results of this study indicate that several areas of closely-related research deserve attention in the future. Specific recommendations include:

1. There continues to be a need for precise experimental measurements of the emittance of engineering solids, particularly at high temperatures. Very little high temperature data is available even for the common metallic elements. The development of experimental methods for the precise measurement of the monochromatic emittance or reflectance of carefully prepared specimens at temperatures to 2500° K or above would contribute considerably to our understanding of these important thermo-physical properties. The present theory might assist in the evaluation of the accuracy of such measurements.

2. The theory can be easily extended to provide the capability of calculating total normal emissivity as a function of temperature. This merely requires integration of the monochromatic values over wavelength.

3. Additional theoretical effort is required to obtain an understanding of the high-frequency contributions of interband transitions to the absorptivity of metals. Such study would be particularly useful in the theoretical study of the properties of the transition metals. Available evidence (36) on the electron specific heat of transition metals indicates that the $s \rightarrow d$ transitions are the most important interband transitions.

4. The role of the Umklapp process in absorption phenomena in metals is worthy of more study than it has received in the present investigation, although this might be beyond the sophistication required in an engineering analysis. U-processes would be expected to influence both electron-electron and electron-phonon interactions.

5. A study of the degree to which the core electrons are influenced by a thermal radiation field might contribute to a theoretical understanding of the small negative temperature coefficient of emissivity observed at very short wavelengths for some metals.

6. The theory does not treat metallic alloys or conductive refractory compounds which are important in many thermal radiation systems. Additional effort in this area is warranted.

The study reported in this thesis, while representing only an initial approach toward an improved theoretical understanding of absorption phenomena in metals, demonstrates that quantum concepts and analytical methods can be used to advantage in a simplified analysis without

involving complications which reduce the engineering utility of the analysis. As is the case with most research, this study has generated a number of questions which deserve further investigations. There appear to be many potentially fruitful avenues along which to direct further studies. The situation encountered is somewhat analogous to that facing Alice when Lewis Carroll wrote:

"Which way ought I to go to get from here?"

"That depends a good deal on where you want to get to," said the Cat.

"I don't much care where-" said Alice.

"Then it doesn't much matter which way you go," said the Cat.

"--So long as I get somewhere," Alice added as an explanation.

"Oh, you're sure to do that," said the Cat, "if you only walk long enough."

APPENDIX I

ATOMIC CHARACTERISTICS OF METALS

The theoretical prediction of the thermal radiation properties of metals requires the use of several atomic parameters which characterize the electronic structure of a particular metal. Except for the alkali and noble metals, the required data are difficult to obtain. Values of the Fermi energy and the electron velocity at the Fermi level, for example, are usually defined in terms of the free electron structure. If interband transitions occur, different values of E_f and v_f are necessary to characterize the various transitions. In order to carry out calculations of the optical and thermal radiation properties utilizing the theory developed in this thesis, it is necessary to have available values for the following atomic properties:

1. The Debye temperature - The characteristic Debye temperature can be determined from either specific heat or electrical resistivity measurements. For most metals the value obtained from specific heat data, θ_D , is not exactly the same as that obtained from resistivity data θ_R . Because our use of the Debye temperature is closely related to its use in resistivity theory, we are interested in values of θ_R . Both θ_D and θ_R are tabulated in Table I-1. The values are those compiled by Meaden (54).

TABLE I-1

Atomic Properties of Metals

Metal	Atomic No. (valence)	Crystal Structure	Melting Point* °K	θ_D^* °K	θ_R^* °K	ρ_{273}^* μΩ-cm	f_{np}		$N \times 10^{-22}$		E_f		$v_F/c \times 10^3$		ρ_0^* μΩ-cm	$C_0 \times 10^{-13}$ sec ⁻¹	$C_e \times 10^{-12}, \text{sec}^{-1}$		$\Gamma_i \times 10^{-15}, \text{sec}^{-1}$	
							ev	Ref	cm ⁻³	Ref	ev	Ref		Ref			Eq. (128)	Used	Eq. (130)	Used
Na	11 (mono.)	bcc	371	160	185	8.494	7.12	9	2.5	9	3.1	9	1.1	9	0.001	8.38	0.08	0.08	0.008	0.008
Mg	12 (dival.)	cph	924	325	340	3.94	15.3	9							0.004				0.12	
Al	13 (trival.)	fcc	933	385	395	2.50	17.7	33	6.0	53	11.8	74	4.7	53	0.0001	77.6	0.07	7.5	0.01	2
Tl	22 (tetra.)	cph	1941	555	342	39.0									0.03				2.4	
Cr	24 (trans.)	bcc	2140	450	485	12.1														
Fe	26 (trans.)	bcc	1807			8.7														
Ni	28 (trans.)	fcc	1726	390		6.2	8.3	80	9.1	85	8.0	86	3.3 ⁺	85	0.02	55.7	0.15	80	0.35	0.5
Cu	29 (mono.)	fcc	1356	320	320	1.55	9.3	33	6.5	53	7.0	9	5.3	53	0.03	13.8	0.21	10	0.67	5
Zn	30 (dival.)	cph	692.6	245	175	5.45	9.8	85							0.005				0.12	
Mo	42 (trans.)	bcc	2890	580		4.8														
Ag	47 (mono.)	fcc	1234	220	200	1.47	9.2	33	5.9	53	5.5	9	4.7	53	0.001	7.67	0.43**	0.43	1.9**	1.9
Sn	50 (tetra.)	---	505.1	165	185	10.1	14	33	3.7	53			4.0	53	0.0001				0.01	
W	74 (trans.)	bcc	3670	315	333	4.8			6.3	53			4.8	53						
Pt	78 (trans.)	fcc	2042	225	240	9.59			6.7	53			4.8	53						
Au	79 (mono.)	fcc	1336	185	200	2.01	9	84	5.9	53	5.5	9	4.7	53	0.001	10.04	1.03**	1.03	1.1**	1.1
Pb	82 (tetra.)	fcc	600.6	98	100	19.5	14	33	5.3	53			5.8	53	0.004				0.20	

* Reference (54)

** Reference (52)

+ s-band electrons

2. The dc resistivity - The dc conductivity (or its reciprocal, the dc resistivity) is required in Eq. (123) to obtain values of the atomic constant C_0 . The functions α and $F_5^0(\alpha)$ are evaluated at 273.15°K for use in Eq. (123); hence, we require the dc resistivity at that temperature. The data compiled by Meaden (54) are listed in Table I-1.

3. The volume plasmon energy - The plasma frequency ω_p is required at several points in the theory. Experimental data of electron plasma oscillations are usually reported in terms of the plasmon energy $\hbar\omega_p$. The plasmon is the quantum excitation representing the quantized plasma oscillations (33). It is analogous to the phonon which represents the quantized lattice vibrations. Values of the plasmon energy, as reported by several authors, are listed in Table I-1.

4. The number of conduction electrons per unit volume - The electron-electron atomic constant, given by Eq. (128), is a function of several atomic parameters including the number of conduction electrons per unit volume N . The values of N given in Table I-1 are mostly those used by Dingle (53) in his analysis of reflectivity.

5. The Fermi energy - The electron kinetic energy at the Fermi level, E_f , also enters into the approximate evaluation of C_e in Eq. (128). The values in Table I-1 for Na, Cu, Ag and Au are those reported by Kittel (9). That for Al is from Pines (33) and the free-electron value for Ni is from Ehrenreich (86).

6. Electron velocity at the Fermi level - The velocity of an electron at the Fermi level, v_f , is required to estimate C_e in Eq. (128) and to estimate the skin absorption from Eq. (132). Values of v_f/c are listed in Table I-1.

7. Residual resistivity - The influence of impurity interactions is estimated from the residual resistivity ρ_0 . Calculation of the approximate impurity damping coefficient using Eq. (130) requires values of both the residual resistivity and the plasma frequency. The values of ρ_0 listed in Table I-1 are those compiled by Meaden (54).

The values of C_0 given in Table I-1 were computed using Eq. (123) and the atomic constants given in the table. The values of C_e and Γ_i were computed from Eqs. (128) and (130), respectively, with the exception of the values for Ag and Au which were taken from the experimental results of Padalka and Shklyarevskii (52). If Eqs. (128) and (130) are used to calculate C_e and Γ_i for Ag and Au, the results are appreciably smaller than the available data. For both metals the computed values are $C_e = 0.08 \times 10^{12}$ and $\Gamma_i = 0.02 \times 10^{13}$. The influence of stationary imperfections would be expected to differ considerably depending on the purity of the specimen and the manner in which it was prepared. Surface imperfections would also have a greater effect on optical measurements, such as those of Padalka and Shklyarevskii, than on bulk measurements of residual resistivity. Since the theory deals

with the optical phenomena, the larger measured values of Γ_1 are undoubtedly more applicable than the computed values.

The discrepancy between the measured and computed values of C_e might be attributed to an underestimation of the electron-electron collision cross-section. As pointed out in the text, improved agreement with experimental data is obtained if values of C_e are used which are more in agreement with the values of Padalka and Shklyarevskii. Unfortunately, very little experimental information is available regarding the electron-electron processes in the other metals. The present theory affords one means of obtaining such data.

APPENDIX II

PERTINENT CONCEPTS OF QUANTUM MECHANICS

This appendix presents a brief outline of the elementary concepts of quantum mechanics as they apply to the subject matter of the thesis. It is intended to serve as a guide to the basic literature for the reader who is unfamiliar with the concepts and application of quantum theory.

The Basic Postulates of Quantum Theory

Quantum mechanics can be regarded as the system of dynamics which attempts to describe fundamental atomic phenomena. Many useful quantum-mechanical relations can be obtained by analyzing a physical system from the viewpoint of classical mechanics and then applying the fundamental postulates of the quantum theory. The most general physical system consists of a group of particles which can interact with each other and respond to external forces. The dynamics of such a system is described in classical mechanics by Hamilton's equations of motion,

$$\frac{\partial p_i}{\partial t} = - \frac{\partial \mathcal{H}}{\partial q_i} ; \quad \frac{\partial p_i}{\partial t} = \frac{\partial \mathcal{H}}{\partial p_i} \quad (1)$$

where the q_i are the coordinates which specify the location of each particle in space and the p_i represent the momenta of the particles. The function \mathcal{H} is the classical Hamiltonian and is a representation of

the total energy of the system (87). According to classical mechanics, the exact state of a system at a future time can be determined by the solution of the Hamilton equations subject to a known set of initial conditions. That is, if the coordinates and momenta of each particle are known for some initial time, all dynamic variables of the system can be calculated exactly for some future time. One of the basic concepts of quantum mechanics is that such a precise specification of the state of a system is impossible. The Heisenberg uncertainty principle of quantum theory asserts that two conjugate variables cannot both be determined with arbitrary precision. The product of the uncertainties of the x-coordinate and x-component of momentum, for example, must obey the inequality

$$\Delta x \Delta p_x \geq \hbar \quad (2)$$

where $\hbar = h/2\pi = 1.054206 \times 10^{-27}$ erg-sec. Therefore, the specification of the state of a system is, according to quantum theory, treated in terms of probabilities. We have the following basic postulates:

Postulate 1. The probability $P(q_i, t)$ that a system will be found with coordinates between q_i and $q_i + dq_i$ at time t is given in terms of a complex state function $\Psi(q_i, t)$,

$$P(q_i, t) dq_1 dq_2 \cdots dq_n = \Psi^*(q_i, t) \Psi(q_i, t) dq_1 dq_2 \cdots dq_n$$

where the asterisk denotes the complex conjugate. The state function is usually normalized such that

$$\int \Psi^* \Psi d\tau = 1$$

where $d\tau$ denotes an element of configuration space.

Postulate 2. For every observable dynamic variable of a system there is associated a corresponding linear hermetian operator \hat{S} . The value of the observable s obtained by a measurement on a system which is in a state described by state function Ψ is given by the expectation value of the corresponding operator

$$\langle \hat{S} \rangle = \int \Psi^* \hat{S} \Psi d\tau$$

The expectation value is a real number because of the hermetian property of the operator,

$$\int \Psi^* \hat{S} \Psi d\tau = \int \Psi (\hat{S} \Psi)^* d\tau$$

Postulate 3. The function $\Psi(q_i, t)$ represents a solution of the time-dependent Schroedinger equation

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (3)$$

where \hat{H} is the quantum-mechanical Hamiltonian operator. The operator is obtained by determining the classical Hamiltonian of the system and replacing each dynamic variable by its corresponding quantum-mechanical operator.

If the Hamiltonian operator does not explicitly depend on time, the state function can be separated

$$\Psi(\vec{r}, t) = u(\vec{r})f(t)$$

Then

$$f(t) = C e^{iEt/\hbar}$$

and the function $u(\vec{r})$ must satisfy the time-independent Schroedinger equation

$$\hat{H}u = Eu \quad (4)$$

This is an eigenvalue equation and the eigenvalue E is the energy of the system. Because the energy does not depend on time (the energy expectation value is equal to the eigenvalue), the system is said to be in a stationary state.

Consider two eigenfunctions u_m and u_n which are solutions of

$$\hat{S}u_m = s_m u_m ; \quad \hat{S}u_n = s_n u_n$$

Then

$$\int [u_n^* \hat{S}u_m - u_m (\hat{S}u_n)^*] d\tau = (s_m - s_n) \int u_n^* u_m d\tau = 0$$

where the last equality is a result of the hermetian property of the quantum operator. Hence, either $s_m = s_n$, in which case the eigenvalues are said to be degenerate, or $\int u_n^* u_m d\tau = 0$, that is, the eigenfunctions are orthogonal. In the degenerate case it is always possible to select linear combinations of the eigenfunctions that are mutually orthogonal. We therefore have the important result that the total set of eigenfunctions of a quantum operator \hat{S} forms a complete orthogonal set. Furthermore, any wave function Ψ which represents a solution of the Schrodinger equation can be expressed as a linear combination of the eigenfunctions of the orthogonal set,

$$\Psi = \sum_{j=0}^{\infty} a_j u_j$$

The expectation value corresponding to the operator \hat{S} for the state with wave function Ψ is

$$\int \Psi^* \hat{S} \Psi dt = \sum_{k=0}^{\infty} a_k^* a_k s_k$$

If the system is in state Ψ and we measure the variable s , the measurement will yield one of the eigenvalues s_j . The probability that the measured value is a particular eigenvalue s_k is proportional to $a_k^* a_k = |a_k|^2$. The matrix element of \hat{S} which connects two states m and n is defined as

$$\int \Psi_m^* \hat{S} \Psi_n dt = \langle m | \hat{S} | n \rangle = S_{mn} \quad (5)$$

The basic concepts of quantum mechanics are discussed in many elementary texts such as Dirac (88), Eyring, Walter and Kimball (89), Schiff (31) and Slater (34).

Stationary Perturbation Theory

Most problems of physical interest are sufficiently complex that exact solutions of the Schroedinger equation cannot be obtained. It is then necessary to utilize approximate methods. One of the most useful techniques is perturbation theory in which a small disturbance applied to the system is treated as a perturbation of the Hamiltonian. We consider first the theory as applied to the approximate solution of the time-independent Schroedinger equation. We assume that the Hamiltonian can be expressed as the sum of two parts: the zero-order, or unperturbed, Hamiltonian H^0 and a perturbation term H' . The zero-order term is selected such that the eigenvalue equation

$$H^0 u_n = E_n u_n$$

is satisfied by known eigenvalues and eigenfunctions. We assume that H' represents a small perturbation and write

$$H = H^0 + \lambda H'$$

where λ is a parameter which is set equal to unity in the final result.

The energy level and wave function are written

$$\Psi = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \dots$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

and substituted into the time-independent Schroedinger equation. Equating coefficients of equal powers of λ we find that $\Psi^{(0)} = u_n$ and $E^{(0)} = E_n$.

The first-order perturbation is obtained by expanding $\Psi^{(1)}$ in terms of the u_n ,

$$\Psi^{(1)} = \sum_n a_n^{(1)} u_n$$

The expansion coefficients are found to be (31)

$$a_k^{(1)} = \frac{H'_{km}}{E_m - E_k} \quad (6)$$

where

$$H'_{km} = \int u_k^* H' u_m d\tau \quad (7)$$

Time-Dependent Perturbation Theory

The problem of concern in this thesis involves a solution of the time-dependent Schroedinger equation. In this case perturbation theory also involves the assumption that the Hamiltonian is the sum of two parts

$$H = H^0 + H' \quad (8)$$

and that the eigenfunctions and eigenvalues of

$$H^0 u_n = E_n u_n$$

are known. Now, however, we proceed by expanding the wave function in terms of the eigenfunctions $u_n e^{-iE_n t/\hbar}$

$$\Psi = \sum_n a_n(t) u_n e^{-iE_n t/\hbar} \quad (9)$$

where the expansion coefficients are functions of time. They are determined by substituting Eq. (9) into the Schroedinger equation, multiplying on the left by u_k^* , integrating over configuration space and noting the orthonormal properties of the eigenfunctions. We find that the time-rate-of change of the expansion coefficients is given by (31)

$$\dot{a}_k^{(0)} = 0 ; \quad \dot{a}_k^{(p+1)} = \frac{1}{i\hbar} \sum_n H'_{kn} a_n^{(p)} e^{i\omega_{kn}t} , \quad p = 0, 1, 2, \dots \quad (10)$$

where

$$\omega_{kn} = \frac{E_k - E_n}{\hbar} \quad (11)$$

If the system is known to be in a particular state u_n before the perturbation H' is applied at $t=0$, then $a_k^{(0)} = \delta_{kn}$ and

$$a_k^{(1)}(t) = \frac{1}{i\hbar} \int_0^t H'_{kn}(t) e^{i\omega_{kn}t} dt \quad (12)$$

Several simplifications are possible if the perturbation Hamiltonian is independent of time except to be initiated at time $t=0$ and terminated at some later time $t=t'$. However, such is not the case for the problem investigated in this thesis.

Perturbation theory is discussed in detail by Schiff (31) and Eyring, Walter and Kimball (89). Its application to radiation problems is treated by Heitler (47).

APPENDIX III

THE UMKLAPP PROCESS

When an electron undergoes a transition from state \vec{k} to state \vec{k}' by the absorption or emission of a phonon of wave vector \vec{q} , momentum is conserved if

$$\vec{k} - \vec{k}' + \vec{q} = \vec{G} \quad (1)$$

where \vec{G} is a vector in the reciprocal lattice. If \vec{a} , \vec{b} and \vec{c} are the primitive axes of the crystal lattice (9), then the reciprocal lattice is defined by the fundamental vectors

$$\vec{A} = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{B} = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

$$\vec{C} = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

Then a vector in the reciprocal lattice is defined as

$$\vec{G} = l\vec{A} = m\vec{B} + n\vec{C} \quad (2)$$

where l , m and n are integers.

In the process described by Eq. (1) there are two distinct cases. First, if $\vec{G} = 0$ the electron-phonon interaction is referred to as a normal process, or N-process. In this case the final total wave vector $\vec{k}' + \vec{q}$ must equal the initial electron wave vector \vec{k} . If a phonon is created ($\vec{k} - \vec{k}' + \vec{q} = 0$) the momentum of the electron is reduced by the amount $\hbar\vec{q}$. If a phonon is absorbed ($\vec{k} - \vec{k}' - \vec{q} = 0$) the electron momentum is increased by $\hbar\vec{q}$. Because the phonon energy is usually much smaller than the electron energy, an electron in an initial state near the Fermi surface will be scattered to another state near the Fermi surface as illustrated in Figure III-1.

The other scattering process, for which $\vec{G} \neq 0$, is termed the Umklapp process, or U-process. Before discussing this type of electron-phonon interaction it is helpful to recall the concept of a Brillouin zone (9). From the study of x-ray propagation in crystals it is known that there are certain wave vectors (that is, certain wavelengths and propagation directions) for which the x-rays satisfy the Bragg relation and total reflection occurs. Because of the concept of wave-particle duality, the same conditions prevail for the propagation of electrons

through a crystal. For certain values of the electron wave vector \vec{k} , Bragg reflection occurs and there exists a discontinuity in the allowed electron energy. The boundaries in k-space within which the electrons have allowed wave vectors are the Brillouin zones. They are concentric about the k-space origin and correspond to allowed energy bands. The first Brillouin zone is formed by constructing planes normal to the reciprocal lattice vectors at their mid-point when the vectors originate at the origin in k-space.

In the Umklapp process an electron is scattered by a phonon and also undergoes a Bragg reflection at the boundary of the Brillouin zone as shown in Figure III-2. An electron initially in state \vec{k} interacts with a phonon of wave vector \vec{q} resulting in the electron state \vec{k}' indicated by the vector PI which terminates near the Fermi surface. The wave vector \vec{k}' is displaced by the reciprocal lattice vector \vec{G} to the final state represented by OF. The Umklapp process can also occur in the electron-electron interaction (39).

Very little information, either quantitative or qualitative, is available concerning the effect of the Umklapp process on absorption phenomena. It is generally thought that they may be important especially at high temperatures where the phonon energy can become appreciable. Gurzhi (50) concludes that no electron-electron interactions occur unless the Umklapp process is present. It is therefore possible that our qualitative inclusion of an electron-electron interaction term includes some

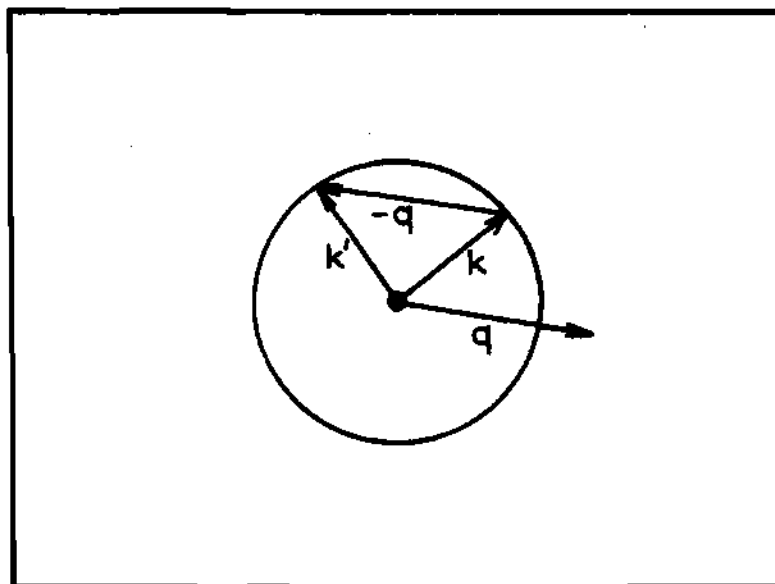


Figure III-1. Normal Scattering of an Electron on a Spherical Fermi Surface in a Cubic Lattice

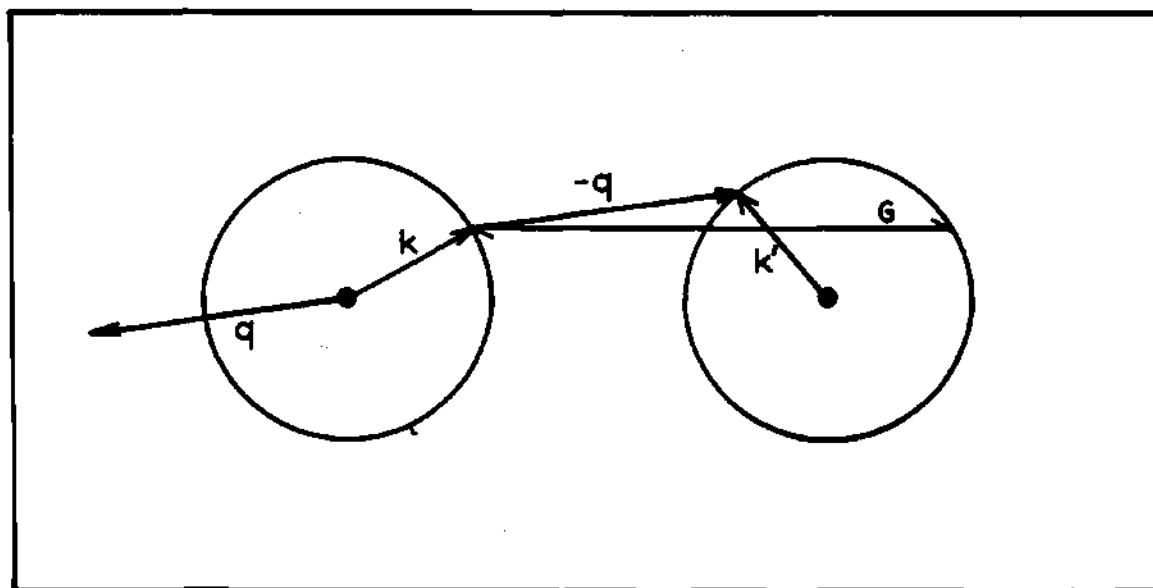


Figure III-2. Umklapp Scattering of an Electron on a Spherical Fermi Surface in a Cubic Lattice

allowance for the Umklapp process. The reader is urged to consult Ziman (39) and Kittel (9) for further discussion of this phenomenon.

APPENDIX IV

MATHEMATICAL CONSIDERATIONS

The absorption and emission of thermal radiation by a metal involves the interactions between the conduction electrons and the photons which represent the external field and between the electrons and the phonons which represent the thermal vibrations of the lattice. In order to obtain an expression for the net amount of energy absorbed by the metal it is necessary to determine the probability that the electron undergoes a transition which involves the absorption or emission of a photon. This requires a solution of the Schroedinger equation for an electron subjected to the perturbing influences of the external electromagnetic field and the lattice potential. This appendix presents the mathematical considerations involved in obtaining an approximate solution of the Schroedinger equation and utilizing the solution to determine energy expenditure of the thermal radiation field. The analysis leads to the theoretical equations presented in Chapter III.

The Perturbation Hamiltonians

According to the model of the atomic system outlined in Chapter III, the conduction electrons are subjected to perturbations described

by four Hamiltonian operators. The first-order perturbation Hamiltonians are:

1. Photon absorption ($\vec{k} \rightarrow \vec{k} + \vec{p}$):

$$H'_1 = \frac{\hbar e \vec{E}_0}{2m^* \omega} e^{i(\vec{p} \cdot \vec{r} - \omega t) \cdot \Delta} \quad (1)$$

2. Photon emission ($\vec{k} \rightarrow \vec{k} - \vec{p}$):

$$H'_2 = \frac{\hbar e \vec{E}_0}{2m^* \omega} e^{i(\vec{p} \cdot \vec{r} - \omega t) \cdot \Delta} \quad (2)$$

3. Phonon absorption ($\vec{k} \rightarrow \vec{k} + \vec{q}$):

$$H'_3 = iE_d \sum_{\vec{q}} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q} e^{i(\vec{q} \cdot \vec{r} - \omega_q t)} \quad (3)$$

4. Phonon emission ($\vec{k} \rightarrow \vec{k} - \vec{q}$):

$$H'_4 = -iE_d \sum_{\vec{q}} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q + 1} e^{-i(\vec{q} \cdot \vec{r} - \omega_q t)} \quad (4)$$

The elements of the transition matrix are defined as

$$H'_{mn} = \int u_m^* H' u_n d\tau \quad (5)$$

where the integration is over configuration space and the normalized electron eigenfunctions are

$$u_{\mathbf{k}} = e^{i\mathbf{k}\cdot\vec{r}} \quad (6)$$

The Bohr frequency relating the energy of an initial state n to that of a final state m is

$$\omega_{mn} = \frac{E_m - E_n}{\hbar} \quad (7)$$

First-Order Transitions

The dynamic equation of the first order perturbation expansion coefficients is (31)

$$\frac{\partial a_m^{(1)}}{\partial t} = \dot{a}_m^{(1)} = \frac{1}{i\hbar} \sum_n H'_{mn} a_n^{(0)} e^{i\omega_{mn}t} \quad (8)$$

The zero-order coefficients are taken to be $a_n^{(0)} = \delta_{mn}$. There are four possible first-order transitions.

Case I ($\vec{k} \rightarrow \vec{k} + \vec{p}$):

The transition matrix element for the absorption of a photon is

$$H'_{k+p,k} = \int u_{k+p}^* H' u_k d\tau = \int e^{-i[(\vec{k}+\vec{p})\cdot\vec{r}]} \left[\frac{\hbar e \vec{E}_0}{2m^* \omega} e^{i(\vec{p}\cdot\vec{r}-\omega t)} \right] e^{i\vec{k}\cdot\vec{r}} d\tau$$

But $\nabla e^{i\vec{k}\cdot\vec{r}} = i\vec{k} e^{i\vec{k}\cdot\vec{r}}$; hence

$$H'_{k+p,k} = i \frac{\hbar e (\vec{E}_0 \cdot \vec{k})}{2m^* \omega} e^{-i\omega t}$$

Thus

$$\dot{a}_{k+p}^{(1)} = \frac{1}{i\hbar} \left[i\hbar \frac{e(\vec{E}_0 \cdot \vec{k})}{2m^* \omega} \right] e^{i(\omega_{k+p,k}-\omega)t} = \frac{e(\vec{E}_0 \cdot \vec{k})}{2m^* \omega} e^{i(\omega_{k+p,k}-\omega)t}$$

and

$$a_{k+p}^{(1)} = \int_0^t \dot{a}_{k+p}^{(1)} dt = \frac{\hbar e (\vec{E}_0 \cdot \vec{k})}{2im^* \omega} \frac{e^{i(\omega_{k+p,k}-\omega)t} - 1}{\hbar(\omega_{k+p,k}-\omega)} \quad (9)$$

Case II ($\vec{k} \rightarrow \vec{k} - \vec{p}$):

The transition matrix element for the emission of a photon is

$$\begin{aligned} H'_{k-p,k} &= \int u_{k-p}^* H' u_k d\tau = \int e^{-i[(\vec{k}-\vec{p})\cdot\vec{r}]} \left[-\frac{\hbar e \vec{E}_0}{2m^* \omega} e^{-i(\vec{p}\cdot\vec{r}-\omega t)} \right] e^{i\vec{k}\cdot\vec{r}} d\tau \\ &= -i \frac{\hbar e (\vec{E}_0 \cdot \vec{k})}{2m^* \omega} e^{i\omega t} \end{aligned}$$

Thus

$$\dot{a}_{\mathbf{k}-\mathbf{p}}^{(1)} = \frac{1}{i\hbar} \left[-i\hbar \frac{e(\vec{E}_0 \cdot \vec{k})}{2m^*\omega} \right] e^{i(\omega_{\mathbf{k}-\mathbf{p},\mathbf{k}+\omega})t} = -\frac{e(\vec{E}_0 \cdot \vec{k})}{2m^*\omega} e^{i(\omega_{\mathbf{k}-\mathbf{p},\mathbf{k}+\omega})t}$$

and

$$a_{\mathbf{k}-\mathbf{p}}^{(1)} = \int_0^t \dot{a}_{\mathbf{k}-\mathbf{p}}^{(1)} dt = -\frac{\hbar e(\vec{E}_0 \cdot \vec{k})}{2im^*\omega} \frac{e^{i(\omega_{\mathbf{k}-\mathbf{p},\mathbf{k}+\omega})t} - 1}{\hbar(\omega_{\mathbf{k}-\mathbf{p},\mathbf{k}+\omega})} \quad (10)$$

Case III ($\vec{k} \rightarrow \vec{k} + \vec{q}$):

The transition matrix element for the absorption of a phonon is

$$\begin{aligned} H'_{\mathbf{k}+\mathbf{q},\mathbf{k}} &= \int u_{\mathbf{k}+\mathbf{q}}^* H' u_{\mathbf{k}} d\tau = \int e^{-i[(\vec{k}+\vec{q}) \cdot \vec{r}]} \left[iE_d \sum_q \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q} \right. \\ &\quad \left. \cdot e^{i(\vec{q} \cdot \vec{r} - \omega_q t)} \right] e^{i\vec{k} \cdot \vec{r}} d\tau = iE_d \sum_q \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q} e^{-i\omega_q t} \end{aligned}$$

Thus

$$\begin{aligned} \dot{a}_{\mathbf{k}+\mathbf{q}}^{(1)} &= \frac{1}{i\hbar} \left[iE_d \sum_q \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q} e^{-i\omega_q t} \right] e^{i(\omega_{\mathbf{k}+\mathbf{q},\mathbf{k}})t} \\ &= \frac{E_d}{\hbar} \sum_q \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q} e^{i(\omega_{\mathbf{k}+\mathbf{q},\mathbf{k}} - \omega_q)t} \end{aligned}$$

and

$$a_{\mathbf{k}+\mathbf{q}}^{(1)} = \int_0^t \dot{a}_{\mathbf{k}+\mathbf{q}}^{(1)} dt = -iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} q \sqrt{n_{\mathbf{q}}} \frac{e^{i(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})t} - 1}{\hbar(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}})}} \quad (11)$$

Case IV ($\vec{k} \rightarrow \vec{k} - \vec{q}$):

The transition matrix element for the emission of a phonon is

$$\begin{aligned} H'_{\mathbf{k}-\mathbf{q}, \mathbf{k}} &= \int u_{\mathbf{k}-\mathbf{q}}^* H'_{\mathbf{q}} u_{\mathbf{k}} d\tau = \int e^{-i[(\vec{k}-\vec{q}) \cdot \vec{r}]} \left[-iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} q \sqrt{n_{\mathbf{q}+1}} \right. \\ &\quad \left. e^{-i(\vec{q} \cdot \vec{r} - \omega_{\mathbf{q}} t)} \right] e^{i\vec{k} \cdot \vec{r}} d\tau = -iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} q \sqrt{n_{\mathbf{q}+1}} e^{i\omega_{\mathbf{q}} t} \end{aligned}$$

Thus

$$\begin{aligned} \dot{a}_{\mathbf{k}-\mathbf{q}}^{(1)} &= \frac{1}{i\hbar} \left[-iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} q \sqrt{n_{\mathbf{q}+1}} e^{i\omega_{\mathbf{q}} t} \right] e^{i\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}} t} \\ &= -\frac{E_d}{\hbar} \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} q \sqrt{n_{\mathbf{q}+1}} e^{i(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}} + \omega_{\mathbf{q}}) t} \end{aligned}$$

and

$$a_{\mathbf{k}-\mathbf{q}}^{(1)} = \int_0^t \dot{a}_{\mathbf{k}-\mathbf{q}}^{(1)} dt = iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} q \sqrt{n_{\mathbf{q}}+1} \frac{e^{i(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}+\omega_{\mathbf{q}}})t-1}}{\hbar(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}+\omega_{\mathbf{q}}})} \quad (12)$$

If we let $\vec{k}' = \vec{k} + \vec{p}, \vec{k} - \vec{p}, \vec{k} + \vec{q}, \vec{k} - \vec{q}$, the first-order coefficients can be written

$$\begin{aligned} a_{\mathbf{k}'}^{(1)} &= \frac{\hbar e(\vec{E}_0 \cdot \vec{k})}{2im^* \omega} \left[\delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}} \left(\frac{e^{i(\omega_{\mathbf{k}+\mathbf{p}, \mathbf{k}-\omega})t-1}}{\hbar(\omega_{\mathbf{k}+\mathbf{p}, \mathbf{k}-\omega})} \right) - \delta_{\mathbf{k}', \mathbf{k}-\mathbf{p}} \right. \\ &\quad \cdot \left(\frac{e^{i(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})t-1}}{\hbar(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})} \right) - iE_d \sum_{\mathbf{q}} \left(\frac{\hbar}{2\rho_p \omega_{\mathbf{q}}} \right)^{1/2} q \left[\delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}} \sqrt{n_{\mathbf{q}}} \right. \\ &\quad \cdot \left. \left. \left(\frac{e^{i(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})t-1}}{\hbar(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})} \right) - \delta_{\mathbf{k}', \mathbf{k}-\mathbf{q}} \sqrt{n_{\mathbf{q}}+1} \left(\frac{e^{i(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})t-1}}{\hbar(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})} \right) \right] \end{aligned} \quad (13)$$

This is Eq. (91) in Chapter III.

Second-Order Transitions

The transitions represented by the first-order coefficients are transitions to virtual states. Absorption and emission of photons by conduction electrons at equilibrium requires second-order transitions, that is, transitions which involve simultaneous photon and phonon processes. The dynamic equation of the second-order perturbation expansion coefficients is (31)

$$\dot{a}_m^{(2)} = \frac{1}{i\hbar} \sum_n H'_{mn} a_n^{(1)} e^{i\omega_{mn}t} \quad (14)$$

where n represents the intermediate states $k + p$, $k - p$, $k + q$, and $k - q$. We consider a specific phonon state and neglect second-order transitions which involve the simultaneous absorption and emission of two photons or two phonons. We must treat four transitions: photon absorption plus phonon absorption ($\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}$), photon absorption plus phonon emission ($\vec{k} \rightarrow \vec{k} + \vec{p} - \vec{q}$), photon emission plus phonon absorption ($\vec{k} \rightarrow \vec{k} - \vec{p} + \vec{q}$) and photon emission plus phonon emission ($\vec{k} \rightarrow \vec{k} - \vec{p} - \vec{q}$). Case I ($\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}$):

The time-rate-of-change of the second-order coefficient for the process which involves the absorption of a photon and a phonon is obtained from Eq. (14). The electron state can be reached either from the $\vec{k} + \vec{p}$ state by the absorption of a phonon or from the $\vec{k} + \vec{q}$ state by the absorption of a photon. Thus

$$\begin{aligned} \dot{a}_{\vec{k}+\vec{p}+\vec{q}}^{(2)} = & \frac{1}{i\hbar} \left[H'_{\vec{k}+\vec{p}+\vec{q},\vec{k}+\vec{p}} a_{\vec{k}+\vec{p}}^{(1)} e^{i\omega_{\vec{k}+\vec{p}+\vec{q},\vec{k}+\vec{p}}t} \right. \\ & \left. + H'_{\vec{k}+\vec{p}+\vec{q},\vec{k}+\vec{q}} a_{\vec{k}+\vec{q}}^{(1)} e^{i\omega_{\vec{k}+\vec{p}+\vec{q},\vec{k}+\vec{q}}t} \right] \end{aligned}$$

The transition matrix elements are

$$H'_{k+p+q, k+p} = \int u_{k+p+q}^* H' z u_{k+p} d\tau = iE_d \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q} e^{-i\omega_q t}$$

$$H'_{k+p+q, k+q} = \int u_{k+p+q}^* H' l u_{k+q} d\tau = \frac{i\hbar e [\vec{E}_0 \cdot (\vec{k} + \vec{q})]}{2m^* \omega} e^{-i\omega t}$$

Thus

$$\begin{aligned} \dot{a}_{k+p+q}^{(2)} &= \frac{e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q} \vec{E}_0 \cdot \left[\frac{\vec{k}}{i\hbar(\omega_{k+p, k} - \omega)} \right. \\ &\quad \cdot \left. \left\{ e^{i(\omega_{k+p+q, k+p} + \omega_{k+p, k} - \omega_q - \omega)t} - e^{i(\omega_{k+p+q, k+p} - \omega_q)t} \right\} \right. \\ &\quad \left. - \frac{i(\vec{k} + \vec{q})}{\hbar(\omega_{k+q, k} - \omega_q)} \left\{ e^{i(\omega_{k+p+q, k+q} + \omega_{k+q, k} - \omega_q - \omega)t} \right. \right. \\ &\quad \left. \left. - e^{i(\omega_{k+p+q, k+q} - \omega)t} \right\} \right] \end{aligned}$$

We note that

$$\hbar(\omega_{k+p+q, k+p} + \omega_{k+p, k}) = E_{k+p+q} - E_{k+p} + E_{k+p} - E_k = \hbar(\omega_{k+p+q, k})$$

$$\hbar(\omega_{k+p+q, k+q} + \omega_{k+q, k}) = E_{k+p+q} - E_{k+q} + E_{k+q} - E_k = \hbar(\omega_{k+p+q, k})$$

We let

$$W_1^{++} = \hbar(\omega_{k+p+q, k+p} + \omega_{k+p, k-\omega_q} - \omega) = \hbar(\omega_{k+p+q, k+q} + \omega_{k+q, k-\omega_q} - \omega)$$

$$W_2^{++} = \hbar(\omega_{k+p+q, k+q} - \omega) \quad ; \quad W_3^{++} = \hbar(\omega_{k+p+q, k+p} - \omega_q)$$

Then

$$\begin{aligned} \dot{a}_{k+p+q}^{(2)} = & -\frac{ie}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q} \vec{E}_0 \cdot \left[\frac{\vec{k}}{\hbar(\omega_{k+p, k-\omega})} \left\{ e^{iW_1^{++} t/\hbar} \right. \right. \\ & \left. \left. - e^{iW_3^{++} t/\hbar} \right\} + \frac{(\vec{k}+\vec{q})}{\hbar(\omega_{k+q, k-\omega_q})} \left\{ e^{iW_1^{++} t/\hbar} - e^{iW_2^{++} t/\hbar} \right\} \right] \end{aligned}$$

and

$$\begin{aligned} a_{k+p+q}^{(2)} = & \int_0^t \dot{a}_{k+p+q}^{(2)} dt = -\frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q} \vec{E}_0 \cdot \left[\left(\frac{(\vec{k}+\vec{q})}{\hbar(\omega_{k+q, k-\omega_q})} \right) \right. \quad (15) \\ & \left. + \frac{\vec{k}}{\hbar(\omega_{k+p, k-\omega})} \left(\frac{e^{iW_1^{++} t/\hbar} - 1}{W_1^{++}} - \frac{(\vec{k}+\vec{q})}{\hbar(\omega_{k+q, k-\omega_q})} \left(\frac{e^{iW_2^{++} t/\hbar} - 1}{W_2^{++}} \right) \right. \right. \\ & \left. \left. - \frac{\vec{k}}{\hbar(\omega_{k+p, k-\omega})} \left(\frac{e^{iW_3^{++} t/\hbar} - 1}{W_3^{++}} \right) \right] \end{aligned}$$

Case II ($\vec{k} \rightarrow \vec{k} + \vec{p} - \vec{q}$):

The state $\vec{k} + \vec{p} - \vec{q}$ can be reached either from $\vec{k} - \vec{q}$ by the absorption of a photon or from $\vec{k} + \vec{p}$ by the emission of a phonon; hence

$$\begin{aligned} \dot{a}_{\vec{k}+\vec{p}-\vec{q}}^{(2)} &= \frac{1}{i\hbar} \left[H'_{\vec{k}+\vec{p}-\vec{q}, \vec{k}+\vec{p}} a_{\vec{k}+\vec{p}}^{(1)} e^{i\omega_{\vec{k}+\vec{p}-\vec{q}, \vec{k}+\vec{p}} t} \right. \\ &\quad \left. + H'_{\vec{k}+\vec{p}-\vec{q}, \vec{k}-\vec{q}} a_{\vec{k}-\vec{q}}^{(1)} e^{i\omega_{\vec{k}+\vec{p}-\vec{q}, \vec{k}-\vec{q}} t} \right] \end{aligned}$$

The transition matrix elements are

$$H'_{\vec{k}+\vec{p}-\vec{q}, \vec{k}+\vec{p}} = \int u_{\vec{k}+\vec{p}-\vec{q}}^* H'_{\vec{k}+\vec{p}} u_{\vec{k}+\vec{p}} d\tau = -ie_d \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q+1} e^{i\omega_q t}$$

$$H'_{\vec{k}+\vec{p}-\vec{q}, \vec{k}-\vec{q}} = \int u_{\vec{k}+\vec{p}-\vec{q}}^* H'_{\vec{k}-\vec{q}} u_{\vec{k}-\vec{q}} d\tau = \frac{i\hbar [\vec{E}_0 \cdot (\vec{k}-\vec{q})]}{2m^* \omega} e^{-i\omega t}$$

Thus

$$\begin{aligned} \dot{a}_{\vec{k}+\vec{p}-\vec{q}}^{(2)} &= \frac{ie}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q+1} \vec{E}_0 \cdot \left[\frac{\vec{k}}{\hbar(\omega_{\vec{k}+\vec{p}, \vec{k}-\omega})} \left\{ e^{iW_1^{+-} t/\hbar} \right. \right. \\ &\quad \left. \left. - e^{iW_3^{+-} t/\hbar} \right\} + \frac{(\vec{k}-\vec{q})}{\hbar(\omega_{\vec{k}-\vec{q}, \vec{k}+\omega_q})} \left\{ e^{iW_1^{+-} t/\hbar} - e^{iW_2^{+-} t/\hbar} \right\} \right] \end{aligned}$$

where

$$W_1^{+-} = \hbar(\omega_{\mathbf{k}+\mathbf{p}-\mathbf{q}, \mathbf{k}+\mathbf{p}} + \omega_{\mathbf{k}+\mathbf{p}, \mathbf{k}} + \omega_{\mathbf{q}, \mathbf{q}-\omega}) = \hbar(\omega_{\mathbf{k}+\mathbf{p}-\mathbf{q}, \mathbf{k}-\mathbf{q}} + \omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}} + \omega_{\mathbf{q}, \mathbf{q}-\omega})$$

$$W_2^{+-} = \hbar(\omega_{\mathbf{k}+\mathbf{p}-\mathbf{q}, \mathbf{k}+\mathbf{p}} - \omega) \quad ; \quad W_3^{+-} = \hbar(\omega_{\mathbf{k}+\mathbf{p}-\mathbf{q}, \mathbf{k}-\mathbf{q}} + \omega_{\mathbf{q}})$$

Then

$$a_{\mathbf{k}+\mathbf{p}-\mathbf{q}}^{(2)} = \frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q + 1} \vec{E}_0 \cdot \left[\left(\frac{\vec{\mathbf{k}} - \vec{\mathbf{q}}}{\hbar(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}} + \omega_q)} + \frac{\vec{\mathbf{k}}}{\hbar(\omega_{\mathbf{k}+\mathbf{p}, \mathbf{k}} - \omega)} \right) \right. \quad (16)$$

$$\cdot \left. \frac{e^{iW_1^{+-} t / \hbar} - 1}{W_1^{+-}} - \frac{\vec{\mathbf{k}} - \vec{\mathbf{q}}}{\hbar(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}} + \omega_q)} \left(\frac{e^{iW_2^{+-} t / \hbar} - 1}{W_2^{+-}} \right) \right.$$

$$\left. - \frac{\vec{\mathbf{k}}}{\hbar(\omega_{\mathbf{k}+\mathbf{p}, \mathbf{k}} - \omega)} \left(\frac{e^{iW_3^{+-} t / \hbar} - 1}{W_3^{+-}} \right) \right]$$

Case III ($\vec{\mathbf{k}} \rightarrow \vec{\mathbf{k}} - \vec{\mathbf{p}} + \vec{\mathbf{q}}$):

The state $\vec{\mathbf{k}} - \vec{\mathbf{p}} + \vec{\mathbf{q}}$ can be reached either from $\vec{\mathbf{k}} - \vec{\mathbf{p}}$ by the absorption of a phonon or from $\vec{\mathbf{k}} + \vec{\mathbf{q}}$ by the emission of a photon; thus

$$\begin{aligned} \dot{a}_{\mathbf{k}-\mathbf{p}+\mathbf{q}}^{(2)} &= \frac{1}{i\hbar} \left[H'_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}-\mathbf{p}} a_{\mathbf{k}-\mathbf{p}}^{(1)} e^{i\omega_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}-\mathbf{p}} t} \right. \\ &\quad \left. + H'_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}+\mathbf{q}} a_{\mathbf{k}+\mathbf{q}}^{(1)} e^{i\omega_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}+\mathbf{q}} t} \right] \end{aligned}$$

The transition matrix elements are

$$H'_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}-\mathbf{p}} = \int u_{\mathbf{k}-\mathbf{p}+\mathbf{q}}^* H'_{\mathbf{z}} u_{\mathbf{k}-\mathbf{p}} d\tau = iE_d \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q} e^{-i\omega_q t}$$

$$H'_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}+\mathbf{q}} = \int u_{\mathbf{k}-\mathbf{p}+\mathbf{q}}^* H'_{\mathbf{z}} u_{\mathbf{k}+\mathbf{q}} d\tau = - \frac{i\hbar e [\vec{E}_0 \cdot (\vec{k}+\vec{q})]}{2m^* \omega} e^{i\omega t}$$

Hence

$$\begin{aligned} \dot{a}_{\mathbf{k}-\mathbf{p}+\mathbf{q}}^{(2)} &= \frac{ie}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q} \vec{E}_0 \cdot \left[\frac{\vec{k}}{\hbar(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})} \left\{ e^{iW_1^- t/\hbar} - e^{iW_3^- t/\hbar} \right\} \right. \\ &\quad \left. + \frac{(\vec{k}+\vec{q})}{\hbar(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_q})} \left\{ e^{iW_1^- t/\hbar} - e^{iW_2^- t/\hbar} \right\} \right] \end{aligned}$$

where

$$W_1^{-+} = \hbar(\omega_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}-\mathbf{p}+\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}-\omega_{\mathbf{q}}+\omega}) = \hbar(\omega_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}+\mathbf{q}+\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}+\omega})$$

$$W_2^{-+} = \hbar(\omega_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}+\mathbf{q}+\omega) \quad ; \quad W_3^{-+} = \hbar(\omega_{\mathbf{k}-\mathbf{p}+\mathbf{q}, \mathbf{k}-\mathbf{p}-\omega_{\mathbf{q}}})$$

Then

$$\begin{aligned} a_{\mathbf{k}-\mathbf{p}+\mathbf{q}}^{(2)} = & \frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q} \vec{E}_0 \cdot \left[\frac{(\vec{\mathbf{k}}+\vec{\mathbf{q}})}{\hbar(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})} + \frac{\vec{\mathbf{k}}}{\hbar(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})} \right] \quad (17) \\ & \cdot \left[\frac{e^{iW_1^{-+} t/\hbar-1}}{W_1^{-+}} - \frac{(\vec{\mathbf{k}}-\vec{\mathbf{q}})}{\hbar(\omega_{\mathbf{k}+\mathbf{q}, \mathbf{k}-\omega_{\mathbf{q}}})} \left(\frac{e^{iW_2^{-+} t/\hbar-1}}{W_2^{-+}} \right) \right. \\ & \left. - \frac{\vec{\mathbf{k}}}{\hbar(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})} \left(\frac{e^{iW_3^{-+} t/\hbar-1}}{W_3^{-+}} \right) \right] \end{aligned}$$

Case IV ($\vec{\mathbf{k}} \rightarrow \vec{\mathbf{k}} - \vec{\mathbf{p}} - \vec{\mathbf{q}}$):

The state $\vec{\mathbf{k}} - \vec{\mathbf{p}} - \vec{\mathbf{q}}$ can be reached either from $\vec{\mathbf{k}} - \vec{\mathbf{p}}$ by the emission of a phonon or from $\vec{\mathbf{k}} - \vec{\mathbf{q}}$ by the emission of a photon; hence

$$\begin{aligned} a_{\mathbf{k}-\mathbf{p}-\mathbf{q}}^{(2)} = & \frac{1}{i\hbar} \left[H'_{\mathbf{k}-\mathbf{p}-\mathbf{q}, \mathbf{k}-\mathbf{p}} a_{\mathbf{k}-\mathbf{p}}^{(1)} e^{i\omega_{\mathbf{k}-\mathbf{p}-\mathbf{q}, \mathbf{k}-\mathbf{p}} t} \right. \\ & \left. + H'_{\mathbf{k}-\mathbf{p}-\mathbf{q}, \mathbf{k}-\mathbf{q}} a_{\mathbf{k}-\mathbf{q}}^{(2)} e^{i\omega_{\mathbf{k}-\mathbf{p}-\mathbf{q}, \mathbf{k}-\mathbf{q}} t} \right] \end{aligned}$$

The transition matrix elements are

$$H'_{k-p-q,k-p} = \int u_{k-p-q}^* H'_{4} u_{k-p} d\tau = - iE_d \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q \sqrt{n_q+1} e^{i\omega_q t}$$

$$H'_{k-p-q,k-q} = \int u_{k-p-q}^* H'_{2} u_{k-q} d\tau = - \frac{i\hbar [\vec{E}_0 \cdot (\vec{k}-\vec{q})]}{2m^* \omega} e^{i\omega t}$$

Thus

$$\begin{aligned} \dot{a}_{k-p-q}^{(2)} = & - \frac{ie}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q+1} \vec{E}_0 \cdot \left[\frac{\vec{k}}{\hbar(\omega_{k-p,k+\omega})} \left\{ e^{iW_1^- t/\hbar} - e^{iW_3^- t/\hbar} \right\} \right. \\ & \left. + \frac{(\vec{k}-\vec{q})}{\hbar(\omega_{k-q,k+\omega_q})} \left\{ e^{iW_1^- t/\hbar} - e^{iW_2^- t/\hbar} \right\} \right] \end{aligned}$$

where

$$W_1^- = \hbar(\omega_{k-p-q,k-p+\omega_{k-p,k+\omega_q+\omega}}) = \hbar(\omega_{k-p-q,k-q+\omega_{k-q,k+\omega_q+\omega}})$$

$$W_2^- = \hbar(\omega_{k-p-q,k-q+\omega}) \quad ; \quad W_3^- = \hbar(\omega_{k-p-q,k-p+\omega_q})$$

Therefore

$$\begin{aligned}
 a_{\mathbf{k}-\mathbf{p}-\mathbf{q}}^{(2)} = & - \frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d \sqrt{n_q + 1} \vec{E}_0 \cdot \left[\left(\frac{(\vec{k}-\vec{q})}{\hbar(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}+\omega_q})} \right. \right. \\
 & + \left. \frac{\vec{k}}{\hbar(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})} \right) \frac{e^{iW_1^- t/\hbar}}{W_1^-} - \frac{(\vec{k}-\vec{q})}{\hbar(\omega_{\mathbf{k}-\mathbf{q}, \mathbf{k}+\omega_q})} \\
 & \cdot \left. \left(\frac{e^{iW_2^- t/\hbar}}{W_2^-} \right) - \frac{\vec{k}}{\hbar(\omega_{\mathbf{k}-\mathbf{p}, \mathbf{k}+\omega})} \left(\frac{e^{iW_3^- t/\hbar}}{W_3^-} \right) \right]
 \end{aligned} \tag{18}$$

If we let

$$B(\mathbf{q}) = b \frac{\hbar e}{2m^* \omega} \left(\frac{\hbar}{2\rho_p \omega_q} \right)^{1/2} q E_d$$

and

$$W_1 = \hbar(\omega_{\mathbf{k}+\mathbf{p}+\mathbf{q}, \mathbf{k}+\omega_q+\omega})$$

$$W_2 = \hbar(\omega_{\mathbf{k}+\mathbf{p}+\mathbf{q}, \mathbf{k}+\mathbf{q}+\omega})$$

$$W_3 = \hbar(\omega_{\mathbf{k}+\mathbf{p}+\mathbf{q}, \mathbf{k}+\mathbf{p}+\omega_q})$$

then the second-order coefficients can be generalized as

$$a_{\vec{k}\pm\vec{p}\pm\vec{q}}^{(2)} = B(q) \left\{ \begin{array}{c} \sqrt{n_q} \\ \sqrt{n_q+1} \end{array} \right\} \vec{E}_0 \cdot \left[\left(\frac{\vec{k}\pm\vec{q}}{\hbar(\omega_{\vec{k}\pm\vec{q},\vec{k}\pm\omega_q})} + \frac{\vec{k}}{\hbar(\omega_{\vec{k}\pm\vec{p},\vec{k}\pm\omega})} \right) \frac{e^{iW_1 t/\hbar-1}}{W_1} \right. \\ \left. - \frac{\vec{k}\pm\vec{q}}{\hbar(\omega_{\vec{k}\pm\vec{q},\vec{k}\pm\omega_q})} \left(\frac{e^{iW_2 t/\hbar-1}}{W_2} \right) - \frac{\vec{k}}{\hbar(\omega_{\vec{k}\pm\vec{p},\vec{k}\pm\omega})} \left(\frac{e^{iW_3 t/\hbar-1}}{W_3} \right) \right] \quad (19)$$

This appears as Eq. (93) in Chapter III. The following table defines the structure of the equation:

<u>Transition</u>	<u>b</u>	<u>Bracket Term</u>	<u>Sign of q</u>	<u>Sign of ω</u>	<u>Sign of ω_q</u>
$\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}$	-1	$\sqrt{n_q}$	$+\vec{q}$	$-\omega$	$-\omega_q$
$\vec{k} \rightarrow \vec{k} + \vec{p} - \vec{q}$	+1	$\sqrt{n_q + 1}$	$-\vec{q}$	$-\omega$	$+\omega_q$
$\vec{k} \rightarrow \vec{k} - \vec{p} + \vec{q}$	+1	$\sqrt{n_q}$	$+\vec{q}$	$+\omega$	$-\omega_q$
$\vec{k} \rightarrow \vec{k} - \vec{p} - \vec{q}$	-1	$\sqrt{n_q + 1}$	$-\vec{q}$	$+\omega$	$+\omega_q$

The Transition Probabilities

The net absorption of photons is a result of terms involving W_1 because the terms in W_2 and W_3 contribute equally to both absorption and emission of photons; hence we need evaluate the transition probability only for those terms containing W_1 . We can therefore write

$$a_{\vec{k}\pm\vec{p}\pm\vec{q}}^{(2)} = B(q) \left\{ \begin{array}{c} \sqrt{n_q} \\ \sqrt{n_q+1} \end{array} \right\} \vec{E}_0 \cdot \left[\frac{\vec{k}\pm\vec{q}}{\hbar(\omega_{\vec{k}\pm\vec{q},\vec{k}\pm\omega_q})} + \frac{\vec{k}}{\hbar(\omega_{\vec{k}\pm\vec{p},\vec{k}\pm\omega})} \right] \frac{e^{iW_1 t/\hbar-1}}{W_1} \quad (20)$$

Consider first the transition $\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}$; the term containing the wave vectors can be written

$$\frac{\vec{k}(\omega_{k+p,k} + \omega_{k+q,k} - \omega_q - \omega) + \vec{q}(\omega_{k+p,k} - \omega)}{\hbar(\omega_{k+q,k} - \omega_q)(\omega_{k+p,k} - \omega)}$$

The coefficient of \vec{k} is

$$\begin{aligned} \hbar(\omega_{k+p,k} + \omega_{k+q,k} - \omega_q - \omega) &= E_{k+p} + E_{k+q} - 2E_k - \hbar\omega_q - \hbar\omega \\ &\approx E_{k+q} - E_k - \hbar\omega_q - \hbar\omega \end{aligned}$$

Thus

$$E_{k+q} - E_k - \hbar\omega_q - \hbar\omega = W_1 - (E_{k+p+q} - E_{k+q}) \approx 0$$

where we have assumed that $|\vec{k}| \gg |\vec{p}|$ and we take $W_1 \approx 0$ except in the resonance terms. It follows that

$$E_{k+q} - E_k - \hbar\omega_q \approx - (E_{k+p} - E_k - \hbar\omega) \approx \hbar\omega$$

We can now write Eq. (20) as

$$a_{\vec{k}+\vec{p}+\vec{q}}^{(2)} = B(q) \sqrt{n_q} \frac{(\vec{E}_0 \cdot \vec{q})}{\hbar \omega} \frac{e^{iW_1 t / \hbar - 1}}{W_1}$$

The transition probability is

$$\begin{aligned} P(\vec{k} \rightarrow \vec{k}+\vec{p}+\vec{q}) &= \lim_{t \rightarrow \infty} \left| a_{\vec{k}+\vec{p}+\vec{q}}^{(2)} \right|^2 \cdot \frac{1}{t} \\ &= |B(q)|^2 n_q \frac{(\vec{E}_0 \cdot \vec{q})^2}{\hbar^2 \omega^2} \lim_{t \rightarrow \infty} \frac{1}{t} \left| \frac{e^{iW_1 t / \hbar - 1}}{W_1} \right|^2 \end{aligned}$$

We make use of the functions $\delta(x)$ and $\xi(x)$ defined as (47)

$$\delta(x) = \lim_{t \rightarrow \infty} \frac{1}{t} \frac{1 - \cos tx}{x^2} = \lim_{t \rightarrow \infty} \frac{1}{\pi} \frac{1}{2t} \left| \xi_t \right|^2$$

$$\xi(x) = \lim_{t \rightarrow \infty} \frac{1 - e^{ixt}}{x}$$

Thus

$$\delta(x) = \lim_{t \rightarrow \infty} \frac{1}{2\pi t} \left| \frac{1 - e^{ixt}}{x} \right|^2 = \lim_{t \rightarrow \infty} \frac{1}{2\pi t} \left| \frac{e^{ixt} - 1}{x} \right|^2$$

We let $z = W_1 / \hbar$ and write

$$\lim_{t \rightarrow \infty} \frac{1}{t} \left| \frac{e^{iW_1 t/\hbar} - 1}{W_1} \right|^2 = \frac{2\pi}{\hbar^2} \lim_{t \rightarrow \infty} \frac{1}{2\pi t} \left| \frac{e^{izt} - 1}{z} \right|^2 = \frac{2\pi}{\hbar^2} \delta(z)$$

But (31) $\delta(ax) = a^{-1}\delta(x)$; hence $\delta(W_1/\hbar) = \hbar\delta(W_1) = \delta(z)$. Thus

$$P(\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}) = \frac{2\pi}{\hbar^3 \omega^2} [B(q)]^2 n_q (\vec{E}_0 \cdot \vec{q})^2 \delta(W_1)$$

This can be generalized to include the other transitions,

$$P(\vec{k} \rightarrow \vec{k} + \vec{q} + \vec{p}) = \frac{2\pi}{\hbar^3 \omega^2} [B(q)]^2 \begin{Bmatrix} n_q \\ n_q + 1 \end{Bmatrix} \delta(E_{\vec{k} + \vec{p} + \vec{q}} - E_{\vec{k}} + \hbar\omega_q + \hbar\omega)$$

The average value of $(\vec{E}_0 \cdot \vec{q})^2$ is

$$\overline{(\vec{E}_0 \cdot \vec{q})^2} = \frac{1}{4\pi} \int E_0^2 q^2 \cos^2 \theta d\Omega = E_0^2 q^2$$

Hence

$$P(\vec{k} \rightarrow \vec{k} + \vec{p} + \vec{q}) = \frac{\pi e^2 E_d^2 E_0^2}{12m^* \omega^4} \frac{1}{\rho_p \omega_q} \begin{matrix} n_q \\ n_q + 1 \end{matrix} \cdot q^4 \delta(E_{\vec{k} + \vec{p} + \vec{q}} - E_{\vec{k}} + \hbar\omega_q + \hbar\omega) \quad (21)$$

The probability of a transition from initial state k to any final state k' is

$$P_r^s(\vec{k}) = 2 \sum_{\vec{k}'} \left[1 - g(E_{\vec{k}'}) \right] P_r^s(\vec{k} \rightarrow \vec{k}')$$

Thus

$$P_r^s(\vec{k}) = \sum_{\vec{k}'} \frac{\pi e^2 E_d^2 E_0^2}{6m^* \omega^4} \left(\frac{1}{\rho_p \omega_q} \right) \left\{ \begin{matrix} n_q \\ n_q + 1 \end{matrix} \right\} q^4 \left[1 - g(E_{\vec{k}'}) \right] \delta(E_{\vec{k}'} - E_{\vec{k}} - \hbar \omega_q - \hbar \omega)$$

The summation over \vec{k}' can be regarded as a summation over \vec{q} because $\vec{k}' \approx \vec{k} \pm \vec{q}$ and the initial states are fixed. Hence, we can replace the sum with a unit volume integral over q ,

$$\sum_{\vec{k}'} \rightarrow \sum_{\vec{q}} \rightarrow \frac{1}{(2\pi)^3} \iiint d^3\vec{q}$$

where $d^3\vec{q} = q^2 dq d\Omega = q^2 dq \sin \gamma d\gamma d\Phi$. The energy relations are spherically symmetric and $\sin \gamma d\gamma = d(\cos \gamma)$. Thus we can write

$$P_r^s(\vec{k}) = \frac{e^2 E_d^2 E_0^2}{48\pi^2 m^* \omega^4} \int_0^{2\pi} d\Phi \int_0^{q_{\max}} q^6 dq \int_{-1}^{+1} d(\cos \gamma) \left(\frac{1}{\rho_p \omega_q} \right) \left\{ \begin{matrix} n_q \\ n_q + 1 \end{matrix} \right\} \cdot \left[1 - g(E_{\vec{k}'}) \right] \delta(E_{\vec{k}'} - E_{\vec{k}} - \hbar \omega_q - \hbar \omega) \quad (22)$$

Transitions can occur only if the argument of the δ -function vanishes for all q such that $0 \leq q \leq q_{\max}$ because the transition probability is non-zero only under such conditions. That is, energy is conserved for the second-order transitions. We can write

$$\begin{aligned} E_{\vec{k}'} - E_{\vec{k}} \mp \hbar\omega_q \mp \hbar\omega &\approx \frac{\hbar^2 |\vec{k} + \vec{q}|^2}{2m^*} - \frac{\hbar^2 k^2}{2m^*} + \hbar\omega_q \mp \hbar\omega \\ &\approx \frac{\hbar^2 q^2}{2m^*} \pm \frac{\hbar^2 kq}{m^*} \cos \gamma \mp \hbar\omega_q \mp \hbar\omega \end{aligned}$$

where $\cos \gamma = \frac{\vec{k} \cdot \vec{q}}{kq}$ and γ is the angle between \vec{q} and \vec{k} . The argument of the δ -function is therefore zero if

$$\begin{aligned} \cos \gamma &= \pm \frac{m^*}{\hbar^2 kq} \left[-\frac{\hbar^2 q^2}{2m^*} \pm \hbar\omega_q \mp \hbar\omega \right] \\ &= \mp \frac{q}{2k} + \frac{m^* \omega q}{\hbar k q} + \frac{m^* \omega}{\hbar k q} \end{aligned}$$

We wish to investigate the relative magnitudes of these terms (86). We can write $\omega_q = v_a q$ where v_a is the acoustic velocity; also, because the electrons are in states near the Fermi level, we have $k \approx v_f m^* / \hbar$. Thus, with $\omega = 2\pi c / \lambda$,

$$\cos \gamma \approx \mp \frac{q}{2k} + \frac{v_a}{v_f} + \frac{2\pi c}{\lambda q v_f}$$

The free-electron velocity at the Fermi surface for metals is $v_f \approx 10^8$ cm/sec.; the acoustic velocity in metals is $v_a \approx 5 \times 10^5$ cm/sec. at room temperature and decreases slightly with increasing temperature. Thus $v_a/v_f < \sim 0.005$. At room temperature and higher, electrons are scattered by phonons in the Debye maximum state $q_0 = (K\theta/\hbar v_a) \approx 10^8$ cm.⁻¹ cm/sec., we can specify the scattering angle such that the argument of the δ -function vanishes,

$$\cos^2 \gamma \leq \left(\frac{q_0}{2k} \right)^2 \leq 1$$

If $q_0 > wk$ the upper limit of integration must be $2k$. We have thus restricted the zeros of the δ -function to lie within the allowable phonon wave vector range. Because the δ -function exhibits a strong maximum at the zero of its argument and is everywhere else nearly zero, we can replace the limits by ∞ and $-\infty$. We can write

$$\begin{aligned} & \int \left[1 - g(E_k') \right] \delta(E_k' - E_k \mp \hbar \omega_q \mp \hbar \omega) d(\cos \gamma) \\ &= \int \left[1 - g(E_k') \right] \delta(E_k' - E_k \mp \hbar \omega_q \mp \hbar \omega) \frac{m^*}{\hbar^2 k q} dE_k' \end{aligned}$$

because $E_{k'} = \frac{\hbar^2}{2m^*} q^2 \pm 2kq \cos \gamma + k^2$; $d(\cos \gamma) = \frac{m^*}{\hbar^2 k q} dE_{k'}$

We have the following relation for the δ -function:

$$\int_{-\infty}^{\infty} f(x) \delta(x-a) dx = f(a)$$

Thus

$$\begin{aligned} & \int_{-\infty}^{\infty} [1-g(E_{k'})] \delta(E_{k'} - E_k \pm \hbar \omega_q \pm \hbar \omega) d(\cos \gamma) \\ &= \frac{m^*}{\hbar^2 k q} [1-g(E_k \pm \hbar \omega_q \pm \hbar \omega)] \end{aligned}$$

We can now write Eq. (22) as

$$P_r^s(\vec{k}) = \frac{eE_d^2 E_0^2}{24\pi \hbar^2 m^* \omega^4} \int_0^{q_{\max}} q^5 \left(\frac{1}{\rho_p \omega_q} \right) \left\{ \begin{matrix} n_q \\ n_q + 1 \end{matrix} \right\} [1-g(E_k, \pm \hbar \omega_q \pm \hbar \omega)] \quad (23)$$

The average value is

$$\overline{P_r^s(\vec{k})} = \frac{\sum_{k'} g(E_{k'}) P_r^s(\vec{k})}{\sum_{k'} g(E_{k'})} \quad (24)$$

The transitions occur near the Fermi level; thus we can convert to energy integrals and use the density of states at the Fermi level (40),

$$\rho(E) = \frac{V(2m^*)^{3/2}}{4\pi^2\hbar^3} E_f$$

Now

$$\int_{-\infty}^{\infty} g(E)\rho(E)dE = N = \frac{V(2m^*)^{3/2}}{3\pi^2\hbar^3} E_f^{3/2}$$

Hence, if we let

$$\beta = 1/KT$$

$$z = \beta(E_k - E_k + \hbar\omega_q + \hbar\omega)$$

$$a = \beta(\hbar\omega_q + \hbar\omega)$$

we have

$$\overline{P_r^s} = \frac{eE_d^2 E_0^2}{32\pi^2 m^* k\omega^4 E_f} \int_0^{q_{\max}} q^5 \left(\frac{1}{\rho_P \omega_q} \right) \left\{ \begin{matrix} n_q \\ n_q + 1 \end{matrix} \right\} dq \cdot \frac{1}{\beta} \int_{-\infty}^{\infty} \frac{1}{(e^{z+a} + 1)} \left(\frac{e^z}{e^z + 1} \right) dz \quad (25)$$

The energy integral can be evaluated in closed form; we let $x = e^z$ and $b = e^a$, then

$$K_r^s = \frac{1}{\beta} \int_{-\infty}^{\infty} \frac{e^z dz}{(e^{z+a}+1)(e^z+1)} = \frac{1}{\beta} \int_0^{\infty} \frac{dx}{(bx+1)(x+1)} = \frac{1}{\beta(b-1)} \ln \frac{bx+1}{bx+b} \Big|_0^{\infty} \quad (26)$$

$$= \frac{1}{\beta} \left(\frac{\ln b}{b-1} \right) = \frac{a}{\beta(e^a-1)}$$

We can now write the transition probability as

$$\overline{P_r^s} = C \int_0^{q_{\max}} q^5 \left(\frac{1}{\rho_p \omega_q} \right) \left\{ \begin{matrix} n_q \\ n_q+1 \end{matrix} \right\} K_r^s dq \quad (27)$$

where

$$C = \frac{e^2 E_d^2 E_0^2}{32\pi \hbar^2 m^* k \omega^4 E_f}$$

The Power Expenditure of the Field

The average power expenditure of the external electromagnetic field can now be written

$$W(\omega, T) = C \sum_s \hbar \omega \int_0^{q_{\max}} q^5 \left(\frac{1}{\rho_p \omega_q} \right) \left\{ \begin{matrix} n_q \\ n_q+1 \end{matrix} \right\} dq \left[K_a^s - K_e^s \right] \quad (28)$$

We note that $\bar{h}\omega_q = \bar{h}v_a q = E_q$. We let

$$\eta = \frac{\bar{h}\omega}{KT}$$

$$\zeta = \frac{\theta}{T}$$

$$x = \frac{v_a q \bar{h}}{KT}$$

Then

$$q_{\max} = \frac{K\theta}{\bar{h}v_a} = \frac{KT}{\bar{h}v_a} x_{\max} ; x_{\max} = \frac{\theta}{T} = \zeta$$

$$\beta \bar{h}(v_a q \bar{h}) = \bar{h}x \bar{h} \eta$$

$$n_q = \frac{1}{e^{\beta E_q} - 1} = \frac{1}{e^{x\eta} - 1}$$

$$n_{q+1} = \frac{e^x}{e^{x\eta} - 1}$$

The power expenditure can then be written

$$W(\omega, T) = C' \frac{1}{v_a} \left(\frac{KT}{\hbar v_a} \right)^5 \left[\int_0^{\zeta} x^4 \left(\frac{1}{e^{x-1}} \right) \frac{1}{\beta} \left\{ \frac{-x-\eta}{e^{-x-\eta-1}} - \frac{-x+\eta}{e^{-x+\eta-1}} \right\} dx \right. \\ \left. + \int_0^{\zeta} x^4 \left(\frac{e^x}{e^{x-1}} \right) \frac{1}{\beta} \left\{ \frac{x-\eta}{e^{x-\eta-1}} - \frac{x+\eta}{e^{x+\eta-1}} \right\} dx \right]$$

where $C' = C\hbar\omega/\rho_p$. After considerable algebraic manipulation, we have

$$W(\omega, T) = \frac{e^2 E_d^2 E_0^2}{32\pi\hbar v_a m^* \rho_p k\omega^3 E_f} \left(\frac{KT}{\hbar v_a} \right)^5 \frac{1}{\beta} \left[(e^{2\eta-1}) F_5(\eta, \zeta) \right. \\ \left. - (e^{\eta-1})^2 \eta F_4(\eta, \zeta) - 2(e^{\eta-1})^2 \eta G_4(\eta, \zeta) \right] \quad (29)$$

where

$$F_n(\eta, \zeta) = \int_0^{\zeta} \frac{x^n dx}{(e^{\eta-e^{-x}})(e^{x-e^{\eta}})}$$

$$G_n(\eta, \zeta) = \int_0^{\zeta} \frac{x^n dx}{(e^{x-1})(e^{\eta-e^{-x}})(e^{x-e^{\eta}})}$$

We have (9)

$$\frac{K\theta}{\hbar v_a} = (6\pi^2 N_p)^{1/3}$$

$$k \approx \frac{1}{\hbar} \sqrt{2m^* E_f}$$

$$\rho = N_p M$$

Thus

$$\frac{e^2 E_d^2 E_0^2}{32\pi \hbar v_a m^* \rho_p k \omega^3 E_f} = \frac{4\pi N e^2}{m^*} \left(\frac{9\pi^2 \hbar^2 N_p E_d^2}{16 \sqrt{2m^* E_f^3} M K \theta} \right) \frac{E_0^2}{\omega^2 N} \zeta^{-5} \frac{1}{2\eta}$$

But

$$\frac{4\pi N e^2}{m^*} = \omega_p^2$$

Thus we can express Eq. (29) as

$$W(\omega, T) = C_0 \frac{E_0^2}{8\pi N} \left(\frac{\omega_p}{\omega} \right)^2 \zeta^{-5} J(\omega, T) \quad (30)$$

where

$$C_0 = \frac{9\pi^3 \hbar^2 N_p E_d^2}{2 \sqrt{2m^* E_f^3} M K \theta} \quad (31)$$

$$J(\omega, T) = \frac{(e^{2\eta} - 1)}{2\eta} F_5(\eta, \zeta) - \frac{1}{2} (e^\eta - 1)^2 F_4(\eta, \zeta) - (e^\eta - 1)^2 G_4(\eta, \zeta) \quad (32)$$

The relation for the power expenditure of the field, given by Eq. (30), appears as Eq. (112) in Chapter III.

APPENDIX V

THE COMPUTER PROGRAMS

The calculations necessary to obtain theoretical values of the optical and thermal radiation properties of metals were carried out with the assistance of a digital computer program. The program was written in FORTRAN V for the UNIVAC 1108 digital computer. It consists of a main program, HETR, and a series of subprograms which are repeatedly called by the main program. The main program and subprograms are as follows:

1. HETR. The main program performs algebraic manipulations on functions supplied by the subprograms to obtain the optical properties and emissivity. It requires the following input:
 - a. the number of elements in the array required by the subprogram DEFINT for integration,
 - b. the electrical resistivity at 273°K in microohm-centimeter,
 - c. the plasmon energy in electron volts,
 - d. the Debye temperature in degrees Kelvin,
 - e. the constant C_e in reciprocal seconds,
 - f. the constant Γ_i in reciprocal seconds,
 - g. the constant skin absorptivity.

This input is different for each metal and is all entered by means of a single card.

The output of the main program consists of:

- a. the plasma frequency in reciprocal seconds,
- b. the value of the function $F_5^{\circ}(\zeta)$ at 273°K,
- c. the constant C_0 in reciprocal seconds,
- d. the dc damping coefficient in reciprocal seconds,

and, for each frequency and temperature:

- e. the value of the parameter η ,
- f. the total damping coefficient in reciprocal seconds,
- g. the optical conductivity in reciprocal seconds,
- h. the dielectric constant,
- i. the index of refraction,
- j. the extinction coefficient, and
- k. the normal monochromatic emissivity.

2. F0N5. This subprogram is an external function which computes values of the function $F_5^{\circ}(\zeta)$ which is defined by Eq. (120) in Chapter III. F0N5 uses subprogram DEFINT.

3. QFACT. This subprogram is an external function which computes the quantum correction factor defined by Eq. (121) in Chapter III. QFACT uses subprograms FUNL and GUNR.

4. FUNL. This subprogram is an external function which computes the function $F_n(\eta, \zeta)$ which is defined by Eq. (114) in Chapter III.

FUNL uses subprogram DEFINT.

5. GUNR. This subprogram is an external function which computes the function $G_n(\eta, \zeta)$ which is defined by Eq. (115) in Chapter III.

GUNR uses subprogram DEFINT.

6. DEFINT. This external function consists of a generalized Simpson's rule routine for integration. It is used to evaluate all integrals.

The relationships of the various subprograms are illustrated in Figure V-1. The extensive use of external functions makes the overall program compact and efficient. Compilation and execution time for a typical run of 14 temperatures and 22 wavelengths at each temperature (2793 output values) is less than 30 seconds on the UNIVAC 1108 computer.

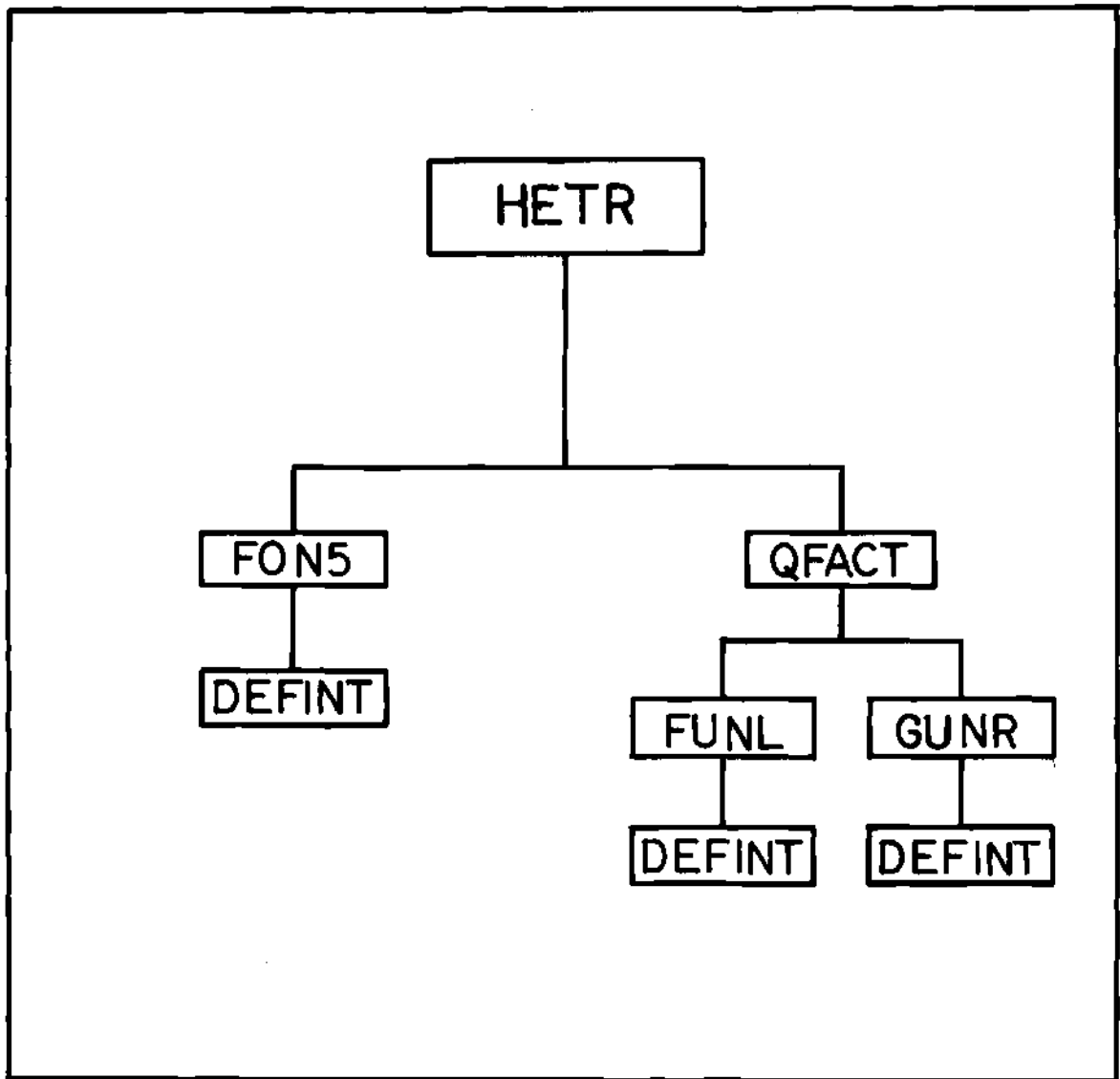


Figure V-1. Computer Program Hierarchy

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1* C THIS PROGRAM COMPUTES THE OPTICAL AND THERMAL RADIATION PROPERTIES
2* C OF METALS FROM QUANTUM ELECTRON PHONON INTERACTION THEORY
3* READ(5,500)N,RES,PLAS,THETA,CEE,GAMD,SKIN
4* 500 FORMAT(1I0,F10.3,2F10.2,E10.2,E10.2,F10.4)
5* WRITE(6,581)
6* 581 FORMAT(1H1,41HOPTICAL AND THER RAD PROPERTIES OF GOLD/)
7* PLF = 1.519498*PLAS
8* BFAC = PLF**2
9* AFAC = BFAC/12.566371
10* ALO = THETA/273.15
11* FAL = FONS(N,ALO)
12* XMIC = (2.569008*RES*(PLAS**2)*(ALO**5))/(12.566371*FAL)
13* XM2 = XMIC*(10.**12)
14* PLF2 = PLF*(10.**15)
15* SIG0 = (89.8758/RES)*(10.**16)
16* GAMO = ((XMIC*FAL)/(ALO**5))*(10.**12)
17* WRITE(6,582)PLF2
18* 582 FORMAT(1H0,20HPLASMA FREQUENCY = ,1PE12.6,3X,7HPER SEC/)
19* WRITE(6,583)SIG0
20* 583 FORMAT(1H0,32HDC CONDUCTIVITY AT 273 DEG K = ,1PE12.6,3X,3HESU/)
21* WRITE(6,584)THETA
22* 584 FORMAT(1H0,25HRESISTANCE DEBYE TEMP = ,F10.2,3X,10HDEG KELVIN/)
23* WRITE(6,585)PLAS
24* 585 FORMAT(1H0,18HPLASMON ENERGY = ,F10.2,3X,2HEV/)
25* WRITE(6,586)FAL
26* 586 FORMAT(1H0,26HDC INTEGRAL AT 273 DEG K = ,1PE12.6/)
27* WRITE(6,587)XM2
28* 587 FORMAT(1H0,19HATOMIC CONSTANT = ,1PE12.6,3X,7HPER SEC/)
29* WRITE(6,588)GAMO
30* 588 FORMAT(1H0,32HDC DAMPING COEF AT 273 DEG K = ,1PE12.6,3X,
31* 1 7HPER SEC//)
32* 504 READ(5,505)T
33* 505 FORMAT(F10,2)
34* WRITE(6,502)T
35* 502 FORMAT(1H1,24HDATA FOR TEMPERATURE = ,F8.2,3X,10HDEG KELVIN//)
36* WRITE(6,503)
37* 503 FORMAT(1H0,2X,4HWAVE,6X,4HFREQ,9X,3HXMU,9X,4HDAMP,12X,3HSIG,10X,
38* 1 6HDIELEC,10X,5HINDEX,11X,4HABCO,11X,4HEMIS//)
39* ALFA = THETA/T
40* XA = XMIC/(ALFA**5)
41* DO 511 I=1,22
42* XI = I
43* IF(I.LE.10)GO TO 561
44* IF(I.GT.10.AND.I.LE.15)GO TO 562
45* IF(I.GT.15.AND.I.LE.17)GO TO 563
46* IF(I.GT.17.AND.I.LE.20)GO TO 564
47* IF(I.GT.20)GO TO 565
48* 561 WAVE = 0.1*XI
49* GO TO 570
50* 562 WAVE = (0.2*XI)-1.
51* GO TO 570
52* 563 WAVE = (0.5*XI)-5.5
53* GO TO 570
54* 564 WAVE = XI-14.0
55* GO TO 570
56* 565 WAVE = (2.*XI)-34.
57* 570 FREQ = 1.883678/WAVE
58* XMU = 7637.752*FREQ/T
59* XOF = QFACT(N,ALFA,XMU)
60* GAME = CEE*(ALFA**(-2))*(1.0+((XMU/6,283185)**2))
61* GAMP = XA*XOF*(10.**(-3))
62* GAM1 = GAMP + GAME + GAMD
63* DEN = (FREQ**2) + (GAM1**2)
64* SIG1 = AFAC*(GAM1/DEN)
65* EPE = 1. - (BFAC/DEN)
66* IF(EPE)506,509,507
67* 506 ZC = -1.
68* GO TO 508
69* 507 ZC = 1.
70* 508 ZA = SQRT(ABS(EPE)/2.)
71* ZB = (12.566371*SIG1)/(FREQ*EPE)
72* ZD = SQRT(1. + (ZB**2))
73* ZN = ZC + ZD
74* ZK = ZD - ZC
75* XREF = ZA*SQRT(ZN)
76* XAB = ZA*SQRT(ZK)
77* EMIS = (4.*XREF)/(((XREF+1.)**2)+(XAB**2)) + SKIN
78* GO TO 510
79* 509 XREF = 0.0
80* XAB = 0.0
81* EMIS = 0.0
82* 510 SIG = SIG1*(10.**15)
83* XOMEG = FREQ*(10.**15)
84* GAM = GAM1*(10.**15)
85* 511 WRITE(6,512)WAVE,XOMEG,XMU,GAM,SIG,EPE,XREF,XAB,EMIS
86* 512 FORMAT(1H0,F6,2,3X,1PE9.3,3X,F9.3,6(3X,1PE12.6))
87* GO TO 504
88* END

```

```

1* C THE FUNCTION FONS EVALUATES AN INTEGRAL
2* FUNCTION FONS(N,ALFA)
3* DIMENSION Y(100)
4* I = 1
5* Y(I) = 0.
6* XN = N-1
7* DX = ALFA/XN
8* DO 103 I=2,N
9* XI = I
10* X = (XI-1.)*DX
11* 103 Y(I) = (X**5)/(EXP(X))/((EXP(X)-1.)**2)
12* FONS = DEFINI(Y,DX,N)
13* RETURN
14* END

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1* C THE FUNCTION OFACT EVALUATES AN ELECTRON PHONON QUANTUM FACTOR
2* FUNCTION OFACT(N,ALFA,XMU)
3* DIMENSION Y(100)
4* IF(XMU.GE.15.)GO TO 403
5* XMUL = (EXP(2.*XMU)-1.)/(2.*XMU)
6* YMUL = (EXP(XMU)-1.)**2
7* NN = 5
8* XA = FUNL(N,NN,ALFA,XMU)
9* NN = 4
10* XB = FUNL(N,NN,ALFA,XMU)
11* XC = GUNR(N,ALFA,XMU)
12* TRM2 = (YMUL*XB)/(2.*XMUL)
13* TRM3 = (YMUL*XC)/XMUL
14* OFACT = XMUL*(XA-TRM2-TRM3)
15* GO TO 405
16* 403 I = 1
17* Y(I) = 0.
18* XN = N-1
19* DX = ALFA/XN
20* DO 404 I=2,N
21* XI = I
22* X = (XI-1.)*DX
23* 404 Y(I) = (X**4)/(EXP(X)-1.)
24* XA = DEFINI(Y,DX,N)
25* XB = (ALFA**5)/10.
26* XC = (ALFA**6)/(12.*XMU)
27* OFACT = XA + XB - XC
28* 405 RETURN
29* END

```

```

1* C THE FUNCTION GUNR EVALUATES AN INTEGRAL
2* FUNCTION GUNR(N,ALFA,XMU)
3* DIMENSION Y(100)
4* I = 1
5* Y(I) = 0.
6* XN = N-1
7* DX = ALFA/XN
8* DO 300 I=2,N
9* XI = I
10* X = (XI-1.)*DX
11* 300 Y(I) = (X**4)/((EXP(X)-EXP(XMU))*(EXP(XMU)-EXP(-X))*(EXP(X)-1.))
12* GUNR = DEFINI(Y,DX,N)
13* RETURN
14* END

```



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1* C THE FUNCTION FUNL EVALUATES AN INTEGRAL
2* FUNCTION F(N,N,ALFA,XMU)
3* DIMENSION Y(100)
4* I = 1
5* Y(I) = 0.
6* XN = N-1
7* DX = ALFA/XN
8* DO 203 I=2,N
9* XI = I
10* X = (XI-1.)*DX
11* 203 Y(I) = (X**N)/((EXP(X)-EXP(XMU))*(EXP(XMU)-EXP(-X)))
12* FUNL = DEFINI(Y,DX,N)
13* RETURN
14* END

```

```

1* C THE FUNCTION DEFINT INTEGRATES USING SIMPSONS RULE
2* FUNCTION DEFINT(Y,DX,N)
3* DIMENSION Y(N)
4* IF(N-3)10,1,2
5* 1 DEFINT = (DX/3.)*(Y(1)+4.*Y(2)+Y(3))
6* RETURN
7* 2 IF(N-4)10,3,4
8* 3 DEFINT = (3.*DX/8.)*(Y(1)+3.*(Y(2)+Y(3))+Y(4))
9* RETURN
10* 4 SEVE = 0.
11* SODD = 0.
12* N1 = N/2
13* N2 = 2*N1
14* M = N
15* NC = M-N2
16* IF(NC.EQ.0) M=N-1
17* NODD = M-1
18* NEVE = M-2
19* DO 7 K=2,NODD,2
20* 7 SODD = SODD+Y(K)
21* DO 8 K=3,NEVE,2
22* 8 SEVE = SEVE+Y(K)
23* DEFINT=(DX/3.)*(Y(1)+Y(M)+4.*SODD+2.*SEVE)
24* IF(NC)10,9,10
25* 9 DEFINT = DEFINT+(DX/24.)*(9.*Y(N)+19.*Y(N-1)-5.*Y(N-2)+Y(N-3))
26* 10 RETURN
27* END

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