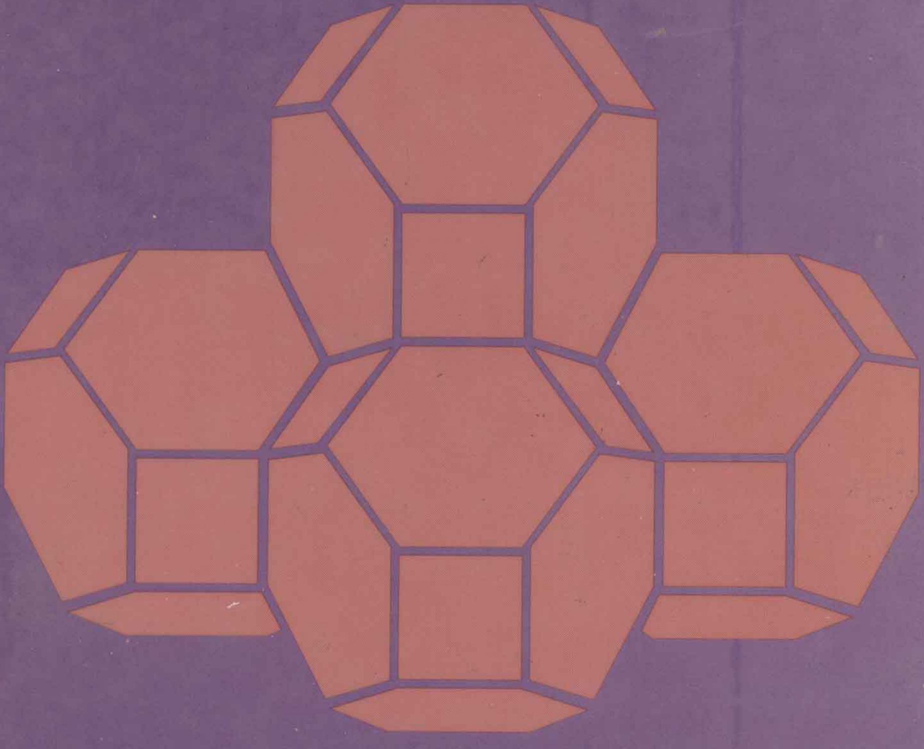
PHYSICAL PROPERTIES of MATERIALS for ENGINEERS

2ND
EDITION

Daniel D. Pollock



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2ND EDITION

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Preface to the Second Edition

This book on the fundamentals of solid state physics is intended for seniors, first-year graduate students of all engineering disciplines, and for self study by practicing technicians and engineers. The intent is to provide for the needs of students and not to impress physicists with elegance and erudition.

The introductory chapters show the limitations of the classical mechanics and the need for a more effective approach to the understanding of the solid state. Elementary quantum mechanics is developed to the extent needed as a basis for the topics that follow.

Topics are introduced by short reviews of prior, relevant materials to orient the reader. The topics then are presented in the least complicated way using unsophisticated mathematics in which all steps are shown and none are considered as being ''obvious''. Alternate explanations are frequently given to promote understanding and to broaden the perspective of the reader. In addition, extensive cross-references are provided to emphasize interrelationships between phenomena and to present a clear, coherent and unified overview of the topics. Illustrations and problems based on commercially available materials are included where appropriate.

The background required is that commonly possessed by engineers and technicians. This includes the equivalents of elementary chemistry, physics, calculus, and physical metallurgy and/or materials science. Information beyond these levels is provided where needed.

This approach is intended to provide maximum accessibility to the understanding of the basic concepts of solid state physics, rather than the ''illusion of knowledge''. It is hoped that this will lead to the selection and utilization of materials at their most effective levels.

Acknowledgments

The practical teachings and physical concepts provided early in my career by Professors C. W. Curtis, of Lehigh University, and F. E. Jaumot, formerly of the University of Pennsylvania, are acknowledged with deep appreciation.

The contributions of Dr. R. P. Reed, of the Sandia National Laboratories, to the chapter on ''Thermoelectric Phenomena'' are noted with many thanks.

I also wish to thank Bonnie Boskat for her assistance in the preparation of the manuscript.

Above all, homage must be paid to *She-Who-Must-Be-Obeyed* for her permission, patience, forbearance and cooperation during the preparation of this book.

Daniel D. Pollock
Williamsville, NY
June, 1992

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CHAPTER 1
Beginnings of Quantum Mechanics

1.1 INTRODUCTION

The topics presented in this chapter are intended to provide a basis for an insight into the nature of quantum effects. It is not intended to describe the selected physical phenomena in detail; as such information is readily available in numerous physics texts. The object is to show how these physical reactions provided the beginnings for quantum mechanics, and, ultimately, to apply the basic concepts to real materials. The historical approach is employed as a means for the gradual introduction of some of the fundamental concepts.

Newtonian, or classical, mechanics are based upon the ideas that the variables of a system, such as energy or momentum, can be precisely known at any given time or position. This general approach leads to the descriptions of the behaviors of systems on *macroscopic* scales. One consequence of this theory permitted Newton to describe geometric optics by considering that a beam of light consisted of a stream of discrete corpuscles.

The Newtonian approach cannot explain diffraction phenomena. The wave theory of the nature of light proposed by Huygens was able to account for these phenomena as well as for geometric optics. Maxwell later showed that light occupied a small portion of the electromagnetic wave spectrum. This led to the wave-particle dilemma that was to play an important part in modern quantum mechanic theory.

1.2 BLACK-BODY RADIATION

All solids and some liquids glow when sufficiently heated (above about 700°C); they give off visible radiation. At lower temperatures this radiation is in the infrared (IR) region and is invisible. The atoms in these solids and liquids are intimately associated so that they are not independent oscillators. This interdependence (see Chapter 4) and interaction results in a continuous spectrum of emitted wavelengths. The radiation from low-pressure gases, where each atom or molecule behaves nearly independently, is discrete and occurs only at the wavelengths of the spectral lines of the gases. Of immediate interest is the visible radiation behavior of heated solids. This is shown schematically in Figure 1-1.

Such spectra are approximately the same for all solids at a given temperature and approach what is known as the *black-body spectrum.* A *perfect black body* is one that absorbs all incident radiation (zero reflectivity). Therefore, all radiation emanating from a black body originates within it. It follows from this that such radiation depends upon the energy of the substance from which it emanates.

The classical attempt at an explanation for this phenomenon is based upon the equipartition of the average energy of each mode of vibration of a group of independent oscillators that constitute the black body, each with its individual frequency. This leads to an expression for the radiant energy per unit volume, $E(\lambda)$, given by

$$E(\lambda) = \frac{8\pi k_B T}{\lambda^4} \tag{1-1}$$

in which k_B is Boltzmann's constant, T is the absolute temperature, and λ is the wavelength of the emitted radiation. This equation cannot explain the curves given in Figure 1-1. At

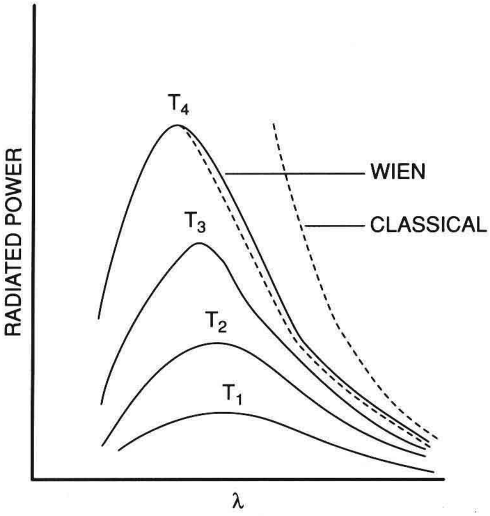

FIGURE 1-1. Radiated power as a function of wavelength for several temperatures: $T_1 < T_2 < T_3 < T_4$. (Modified from Richtmyer, F. K., Kennard, E. H., and Lauritsen, T., *Introduction to Modern Physics*, 5th ed., McGraw-Hill, New York, 1955, 131. With permission.)

very long wavelengths, however, Equation 1-1 does approach agreement with the experimental data.

It will be noted (Figure 1-1) that the wavelengths corresponding to the maxima, λ_M, vary inversely with increasing temperature. This may be stated as

$$\lambda_M T = \text{const.} \tag{1-2}$$

and is known as the *Wien displacement law*; it is one of the bases of optical pyrometry. This property has had a long history of use in the empirical estimation of temperatures by the color of a heated piece of metal, long before physics became a science.

When the radiated energies are compared at different temperatures, the maximum energy is found to vary as T^5, or, where $g(\lambda_M, T)$ is a function of λ_M and T, as

$$E_{max} = g(\lambda_M, T)T^5 \tag{1-3}$$

or, because λ and T are inversely related, where h (λ,T) is a function of λ and T, as

$$E_{max} = \frac{h(\lambda, T)}{\lambda_M^5} \tag{1-4}$$

Wien suggested that this behavior could be given more closely by

$$E_{max} = \frac{C_1}{\lambda_M^5} \cdot \frac{1}{e^{C_2/\lambda T}} \tag{1-5}$$

The curve-fitting constants C_1 and C_2 are empirical and are not defined. This relationship can be made to accurately fit the observed data from the region of the shorter to the maximum wavelengths. Equation 1-5 does not give a good fit to the experimental data in the range from the maximum to the longer wavelengths. Despite this shortcoming, Wien's work constituted a significant advance.

These attempts to understand black-body radiation relate the radiated energy to the temperature of the emittor and to the wavelength of the radiation. These are the obvious factors. The significance of the wavelength is not obvious. Its importance arises from the fact that the radiation depends on the energy of the emitting substance. This, as shown in Section 1.3, can be given only in terms of the frequency of the particles of which it is composed. These two factors are related by $\lambda\nu = c$, where ν is the frequency of the oscillator and c is the speed of light.

1.3 PLANCK'S LAW

Planck was not only able to overcome the difficulties encountered by his predecessors, but included their findings as special cases of his analysis. This was done by a radically new approach to the problem.

Planck (1901) considered that the radiating surface was composed of electric dipole oscillators, and that a relationship should exist between the energy of the radiation and the frequency of the oscillators. Implicit in all of the prior classical work was the idea that the energy of an oscillator could vary only in a continuous energy spectrum. Planck's revolutionary hypothesis was that such energies had to be discrete. His assumptions were that:

1. The energy of an oscillator is of the form

$$E = nh\nu \tag{1-6}$$

   where n is an integer, h is the constant of proportionality, now known as Planck's constant ($h = 6.626 \times 10^{-27}$ erg-s), and ν is the frequency of the oscillation. This means that the energy of the oscillator can no longer be considered as continuous, but can only take on discrete values determined by the integer n.
2. Because the energy of an oscillator is discrete, any transitions from one energy level to another must be associated with the absorption or emission of energy.
3. Any energy gained or lost in such transitions must be in discrete, or quantum, amounts as determined by the integer n.

These assumptions constituted a revolutionary departure from the classical approach that became one of the bases of modern physics. They were to have far-reaching consequences.

When the number of vibrational modes that can be assumed by an oscillator is taken into account along with the average energy of each mode, it is found that

$$E(\lambda, T)\, d\lambda = \frac{8\pi\, d\lambda}{\lambda^4} \cdot \frac{h\nu}{e^{h\nu/k_BT} - 1}$$

where k_B is Boltzmann's constant. Or, recalling that $\lambda\nu = c$ and substituting for ν, gives the radiated energy as

$$E(\lambda, T) = \frac{8\nu ch}{\lambda^5} \cdot \frac{1}{e^{ch/\lambda k_BT} - 1} \tag{1-7}$$

The general expression, ''Planck's law'', gives a very good fit with the observed data over a wide range of wavelengths. It relates the energy associated with any temperature and wavelength, not just with that of the wavelength of the maximum energy. For small values of λ and/or T, $\exp(ch/\lambda k_BT) \gg 1$, thus, Equation 1-7 approaches Equation 1-5. The significant difference is that the constants now are defined as $C_1 = 8\pi ch$ and $C_2 = ch/k_B$. For large values of λ and/or T the exponential term is small, so that the denominator of Equation 1-7 may be approximated by a series approximation for e^x as

$$e^x - 1 \cong x + 1 - 1; \qquad x = \frac{ch}{\lambda k_B T}$$

As a result of this substitution, Equation 1-7 takes the form

$$E(\lambda, T) = \frac{8\pi ch}{\lambda^5} \cdot \frac{\lambda k_B T}{ch} = \frac{8\pi k_B T}{\lambda^4} \tag{1-8}$$

Equation 1-8 is the same as Equation 1-1, obtained by classical means. Therefore, for suitable large values of λ and/or T, the quantum expression reduces to the classical equation.

The significance of this work is that the assumption of a discrete energy behavior, rather than that of a continuous spectrum, results in a expression for black-body radiation that is valid for the entire range of the observed behavior. This result could not have been obtained on the basis of a continuous energy spectrum. The concept of discrete rather than of continuous behavior became the basis for explanations of the other physical effects and now is one of the fundamental concepts of quantum mechanics.

1.4 PHOTOELECTRIC EFFECT

Hertz (1887) found that ultraviolet (UV) light from an electric arc made it easier (required a lower voltage) for sparks to jump across a gap between two other irradiated electrodes in another nearby circuit. It now is known that the electrons that are emitted from the surface of a material, when irradiated by light of suitable wavelength, are responsible for this phenomenon. When a suitable voltage (potential difference) exists between a pair of electrodes, the radiation-generated electrons emitted by one electrode will flow to the other electrode. Lower voltages are required to strike an arc between the electrodes when such radiation-induced electron flows take place between them. The behavior observed by Hertz is a result of the *photoelectric effect.*

For simplicity it is assumed that the electron emitter is an elemental metal. Electrons are not normally emitted from the surface of a metal unless sufficient external energy is added. This energy increment may be in the form of radiant or thermal energy (thermionic emission).

The volume of a metal may be considered as constituting a lower energy environment for its freely moving electrons than that external to its surface. If this were not the case, electrons would not require an additional energy increment for their emission from the metal. This situation is idealized as shown schematically in Figure 1-2. According to this figure, the most energetic electron within the metal would require a minimum increment of energy equal to W in order to leave the metal. W is known as the work function and is a constant for a given, clean metal surface; it is different for each metal (see also Figure 3-4b). The work function also is commonly designated by ϕ.

According to classical theory, the electric field associated with the incident radiation should excite, or remove, the electron from the metal, if it is strong enough. Thus, if the kinetic energy increment that the radiation imparts to the electron is at least equal to W, the electron will be emitted. It was originally thought that the greater the intensity of the incident radiation, the greater the kinetic energy imparted to the emitted electrons. Additionally, because W is the minimum increment of energy required for electron emission, a lower intensity limit should exist below which no electrons could be emitted. On this basis, the kinetic energy of the emitted electrons was expected to be only a function of the intensity of the radiation. As will be shown, this was in error. The kinetic energy of the emitted electrons actually is a function of the frequency of the incident radiation.

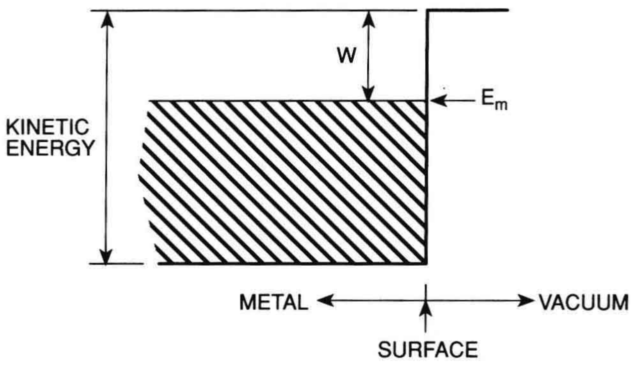

FIGURE 1-2. Work function, W, and energy barrier at the surface of a metal.

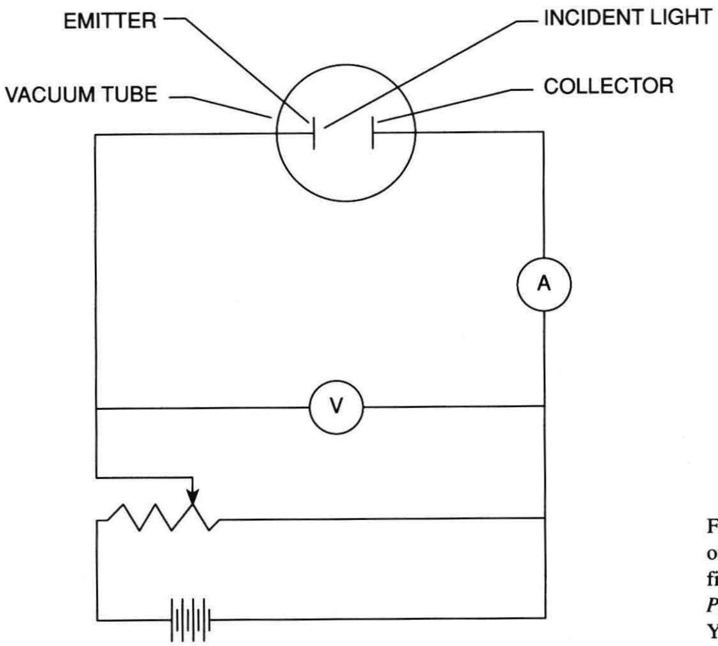

FIGURE 1-3. Schematic diagram of photoelectric apparatus. (Modified from Sproull, R. L., *Modern Physics*, John Wiley & Sons, New York, 1956, 76. With permission.)

Observations of the photoelectric effect can be made with apparatus similar to that shown schematically in Figure 1-3. This apparatus permits the application of either a retarding or an accelerating voltage to be applied between the electrodes in the vacuum tube. The retarding voltage, V, can be varied and adjusted so that $eV = K.E. \geq W$, where e is the charge on an electron and K.E. is its kinetic energy as a result of irradiation. In other words, the retarding voltage can be made to be such that the electrical energy between the electrodes would just balance the kinetic energy of the irradiated electrons so that no electrons would be emitted and no current would flow between the electrodes. This provides a direct measure of the kinetic energy imparted to the electrons by the radiation.

Using monochromatic incident light directed upon the emitter, and varying its intensity, the results shown in Figure 1-4 are observed. As the negative retarding voltage is increased from zero, fewer electrons can reach the collector. A voltage, V_o, is reached at which no electrons can leave the emitter. This gives the maximum kinetic energy of the electrons as eV_o. As the intensity of the monochromatic light is increased, V_o remains constant. The number of emitted electrons multiplies as the intensity grows, increasing the current in the