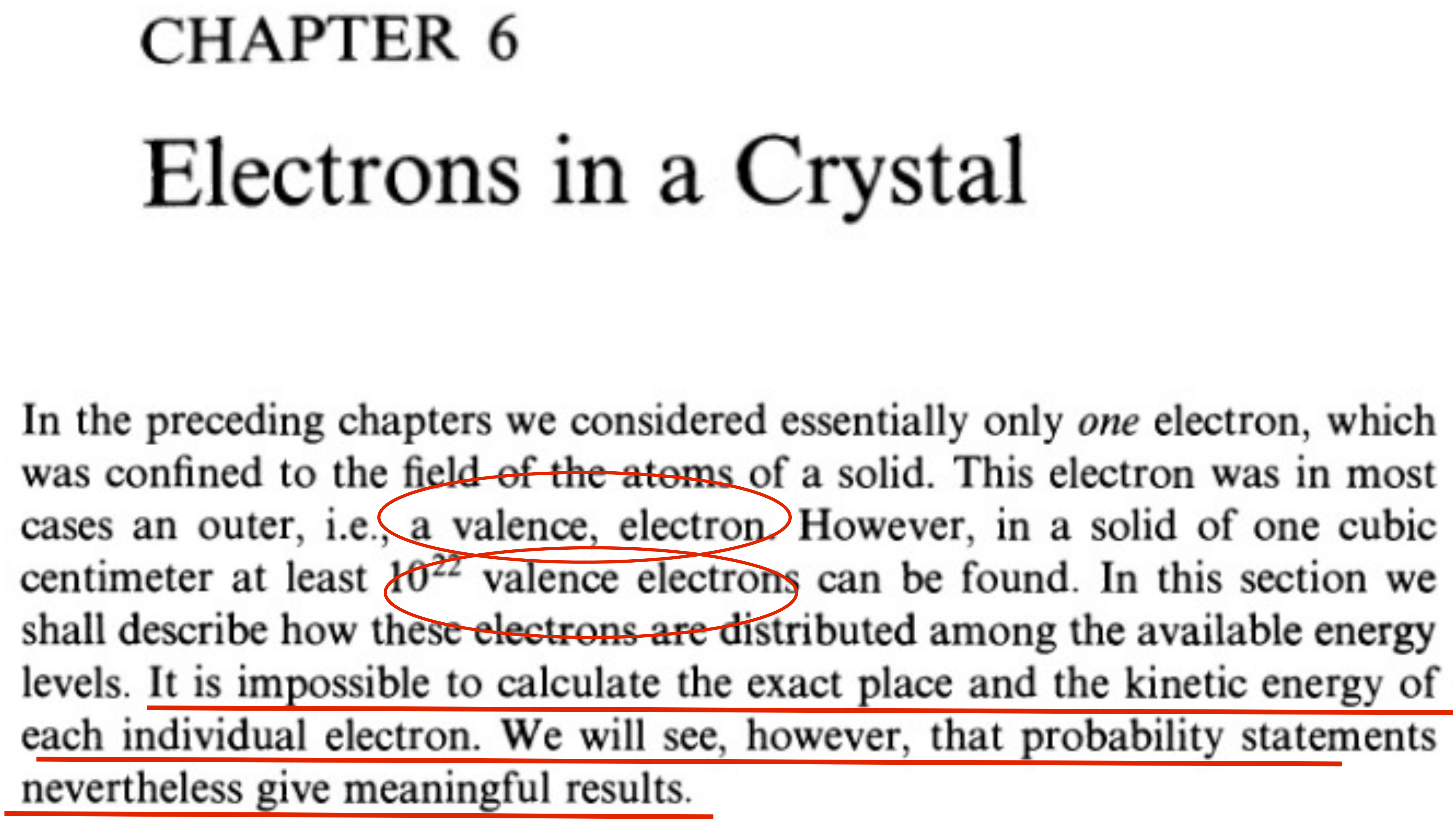


CHAPTER 6

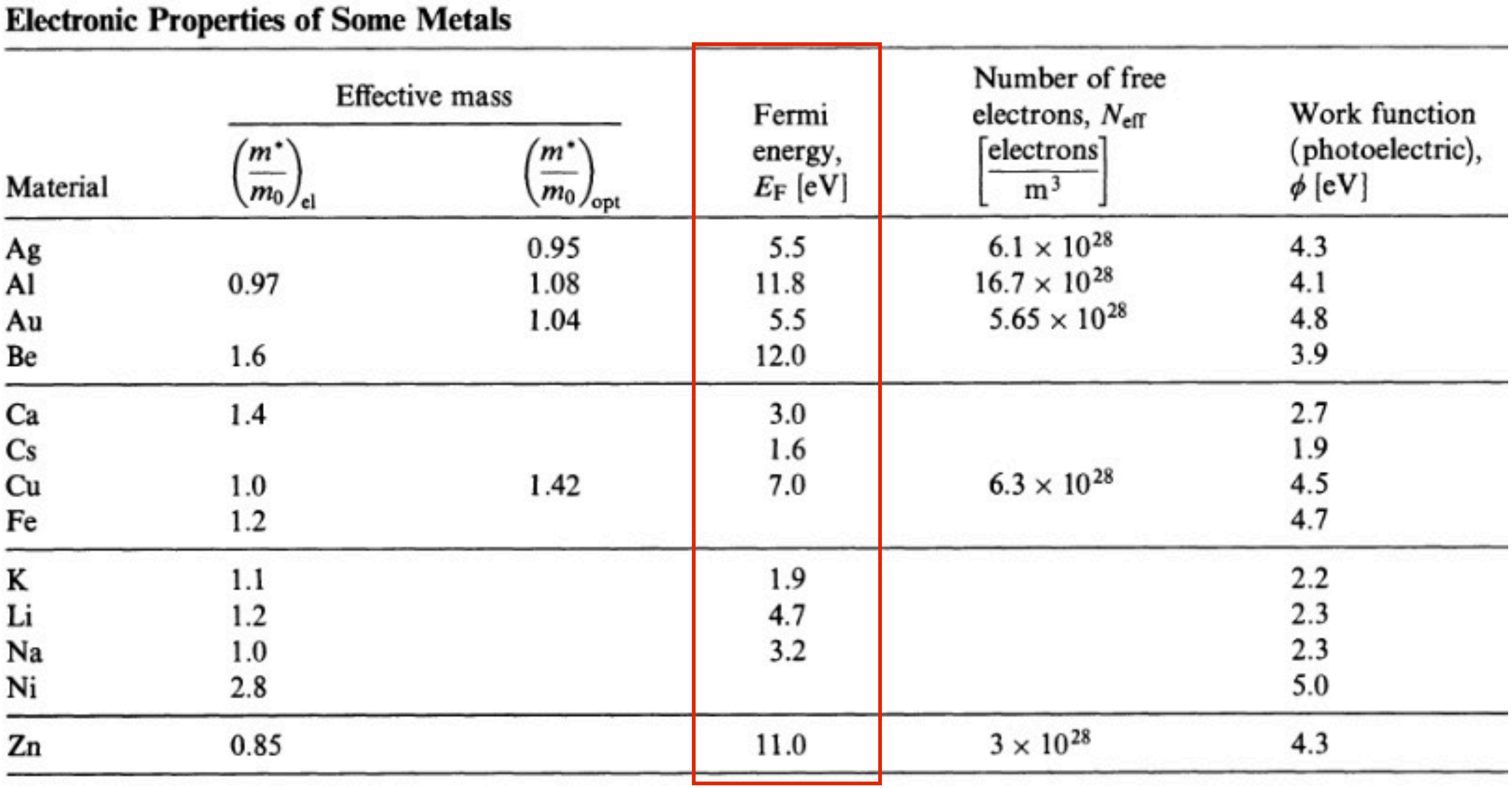
Electrons in a Crystal

In the preceding chapters we considered essentially only *one* electron, which was confined to the field of the atoms of a solid. This electron was in most cases an outer, i.e., a valence, electron. However, in a solid of one cubic centimeter at least 10^{22} valence electrons can be found. In this section we shall describe how these electrons are distributed among the available energy levels. It is impossible to calculate the exact place and the kinetic energy of each individual electron. We will see, however, that probability statements nevertheless give meaningful results.

6.1. Fermi Energy and Fermi Surface

The Fermi energy is often defined as the "highest energy that the electrons assume at $T = 0$ K.

Many of the electronic properties of materials, such as optical, electrical, or magnetic properties, are related to the location of E_F within a band. They range typically from 2 eV to 12 eV



Electronic Properties of Some Metals

Material	Effective mass		Fermi energy, E_F [eV]	Number of free electrons, N_{eff} $\left[\frac{\text{electrons}}{\text{m}^3}\right]$	Work function (photoelectric), ϕ [eV]
	$\left(\frac{m^*}{m_0}\right)_{el}$	$\left(\frac{m^*}{m_0}\right)_{opt}$			
Ag		0.95	5.5	6.1×10^{28}	4.3
Al	0.97	1.08	11.8	16.7×10^{28}	4.1
Au		1.04	5.5	5.65×10^{28}	4.8
Be	1.6		12.0		3.9
Ca	1.4		3.0		2.7
Cs			1.6		1.9
Cu	1.0	1.42	7.0	6.3×10^{28}	4.5
Fe	1.2				4.7
K	1.1		1.9		2.2
Li	1.2		4.7		2.3
Na	1.0		3.2		2.3
Ni	2.8				5.0
Zn	0.85		11.0	3×10^{28}	4.3

6.2. Fermi Distribution Function

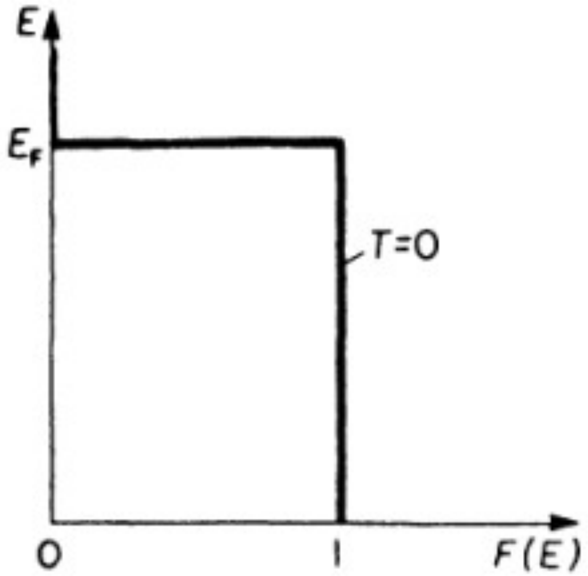
The kinetic energy of an electron gas is governed by Fermi–Dirac statistics, which states that the probability that a certain energy level is occupied by electrons is given by the **Fermi function, F(E)**,

$$F(E) = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}.$$

k_B is the Boltzmann constant, and T is the absolute temperature.

If an energy level E is completely occupied by electrons, the Fermi distribution function F(E) equals 1 (certainty)

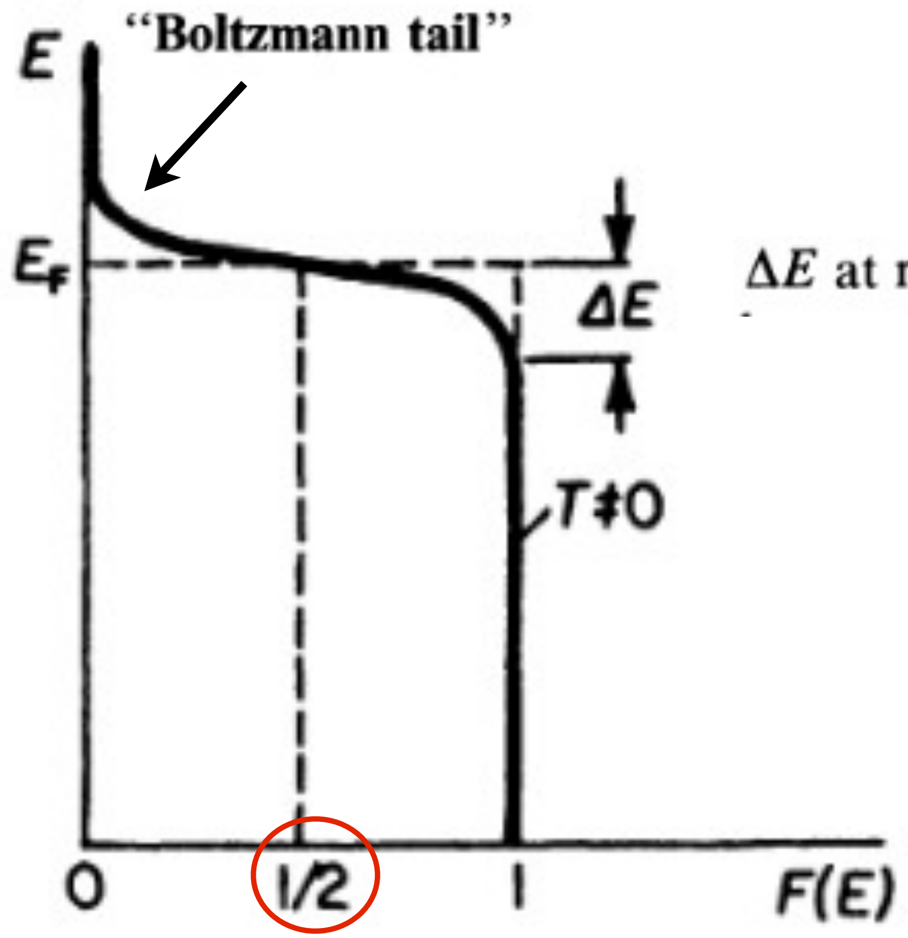
for an empty energy level one obtains F(E) = 0.



One sees from this figure that at $T = 0$ all levels that have an energy smaller than E_F are completely filled with electrons, whereas higher energy states are empty.

At high energies ($E \gg E_F$) the upper end of the Fermi distribution function can be approximated by the classical (Boltzmann) distribution function.

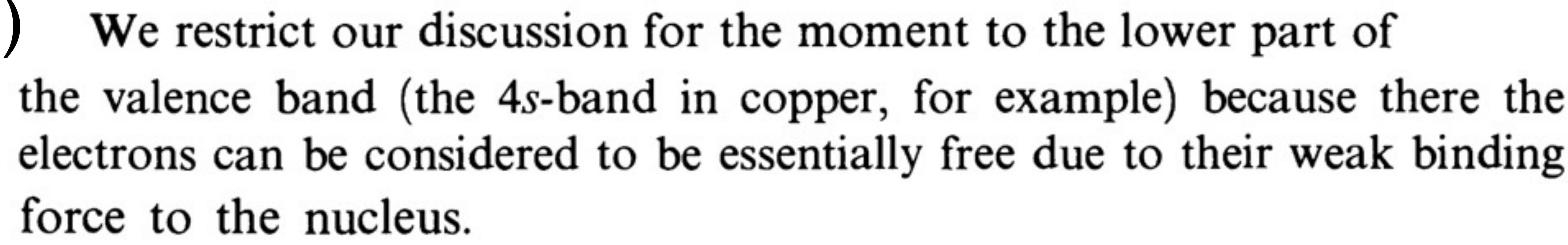
$$F(E) \approx \exp\left[-\left(\frac{E - E_F}{k_B T}\right)\right].$$



ΔE at room temperature is in reality only about 1% of E_F.

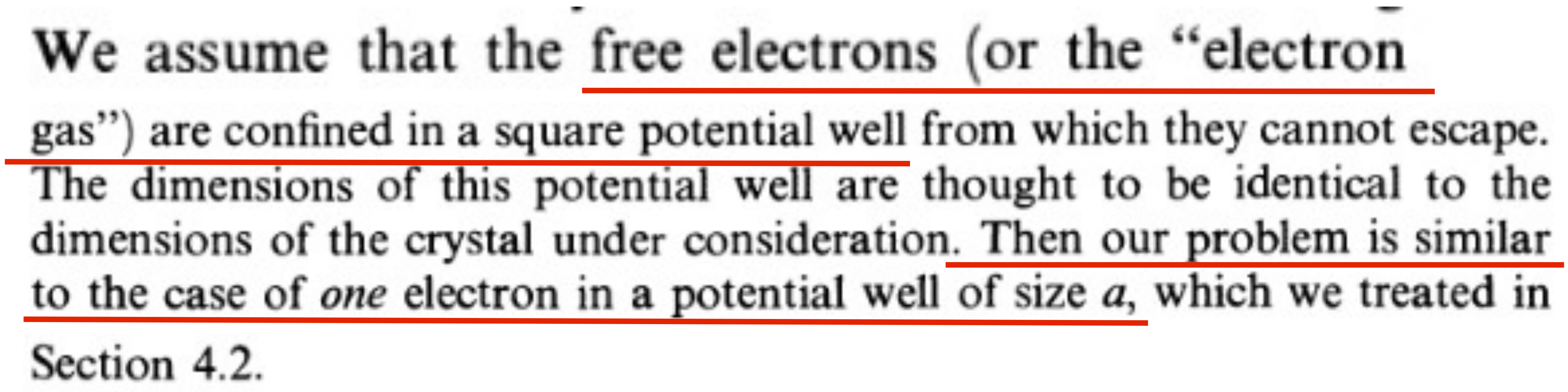
6.3. Density of States

(1)



We restrict our discussion for the moment to the lower part of the valence band (the 4*s*-band in copper, for example) because there the electrons can be considered to be essentially free due to their weak binding force to the nucleus.

(2)



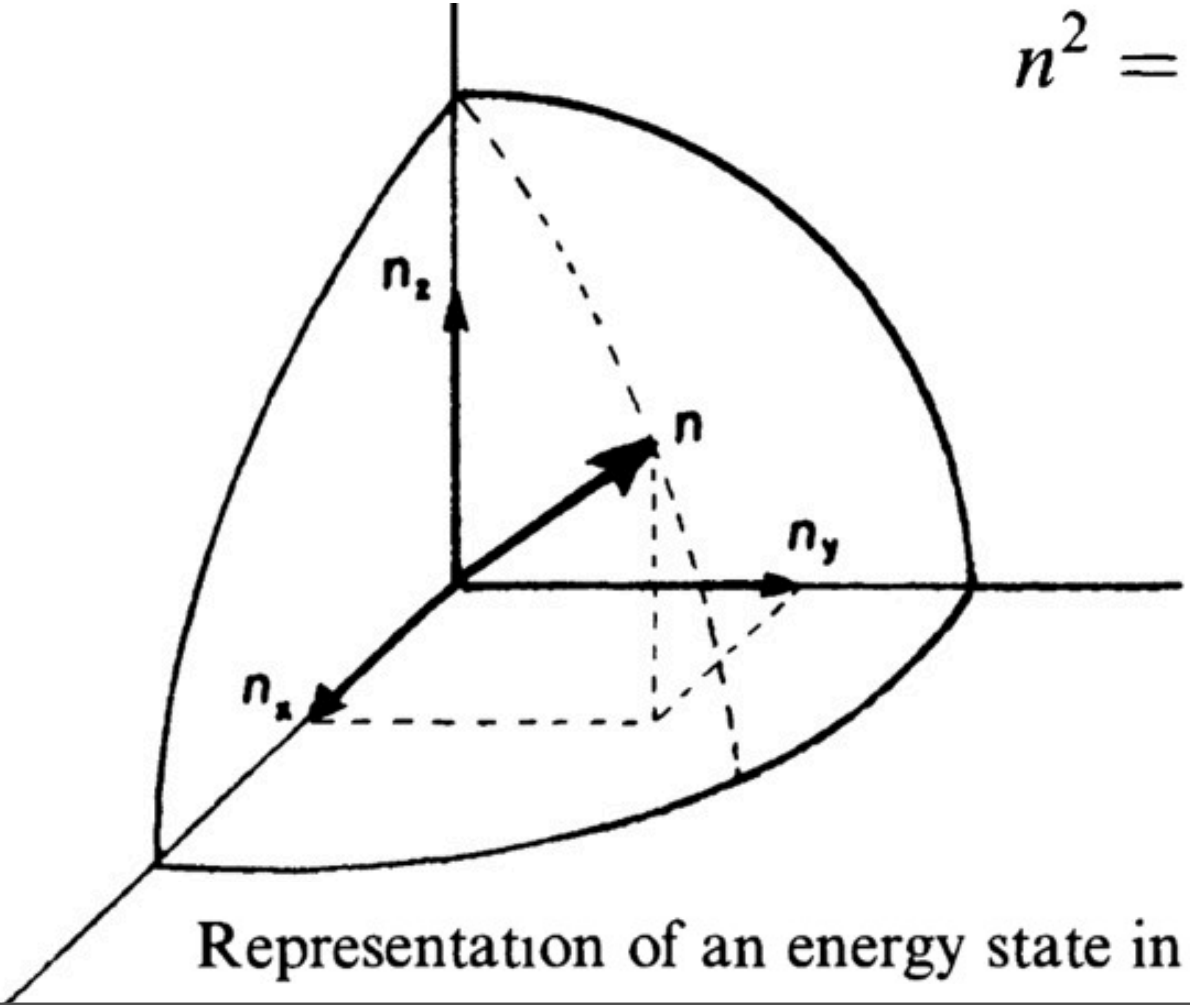
We assume that the free electrons (or the "electron gas") are confined in a square potential well from which they cannot escape. The dimensions of this potential well are thought to be identical to the dimensions of the crystal under consideration. Then our problem is similar to the case of *one* electron in a potential well of size *a*, which we treated in Section 4.2.

$$E_n = \frac{\pi^2 \hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)$$ **“energy state.”**

where n_x, n_y, and n_z are the principal quantum numbers and a is now the *length*, etc., of the crystal. Now we pick an arbitrary set of quantum numbers

n is the radius from the origin of the coordinate system to a point (n_x, n_y, n_z) where

$$n^2 = n_x^2 + n_y^2 + n_z^2$$



Representation of an energy state in quantum number space.

Equal values of the energy E_n lie on the surface of a sphere with radius n.

points within the sphere therefore represent quantum states with energies smaller than E_n. The number of quantum states, η, with an energy equal to or smaller than E_n is proportional to the volume of the sphere.

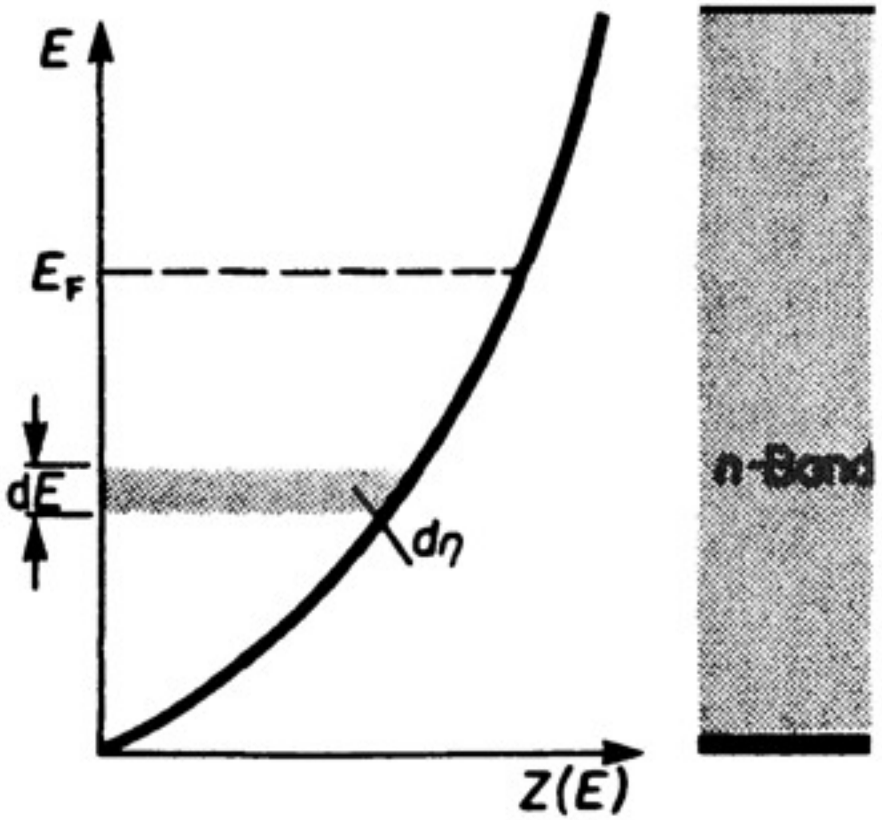
quantum numbers are positive integers, the n-values can only be defined in the positive octant of the n-space. One-eighth of the volume of the sphere with radius n therefore gives the number of energy states, η, the energy of which is equal to or smaller than E_n.

$$\eta = \frac{1}{8} \cdot \frac{4}{3} \pi n^3 = \frac{\pi}{6} \left(\frac{2ma^2}{\pi^2 \hbar^2} \right)^{3/2} E^{3/2}$$

Differentiation of η with respect to the energy E provides the **number of energy states per unit energy** in the energy interval dE, i.e., the density of the energy states, briefly called **density of states**, $Z(E)$:

$$\frac{d\eta}{dE} = Z(E) = \frac{\pi}{4}\left(\frac{2ma^2}{\pi^2\hbar^2}\right)^{3/2} E^{1/2} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

a^3 is the volume, V, that the electrons can occupy



$$d\eta = Z(E) \cdot dE$$

Density of states $Z(E)$ within a band. The electrons in this band are considered to be free.

6.4. Population Density

The number of electrons per unit energy, $N(E)$, within an energy interval dE can be calculated by multiplying the number of possible energy levels, $Z(E)$, by the probability for the occupation of these energy levels. We have to note, however, that because of the **Pauli principle**, each energy state can be occu-

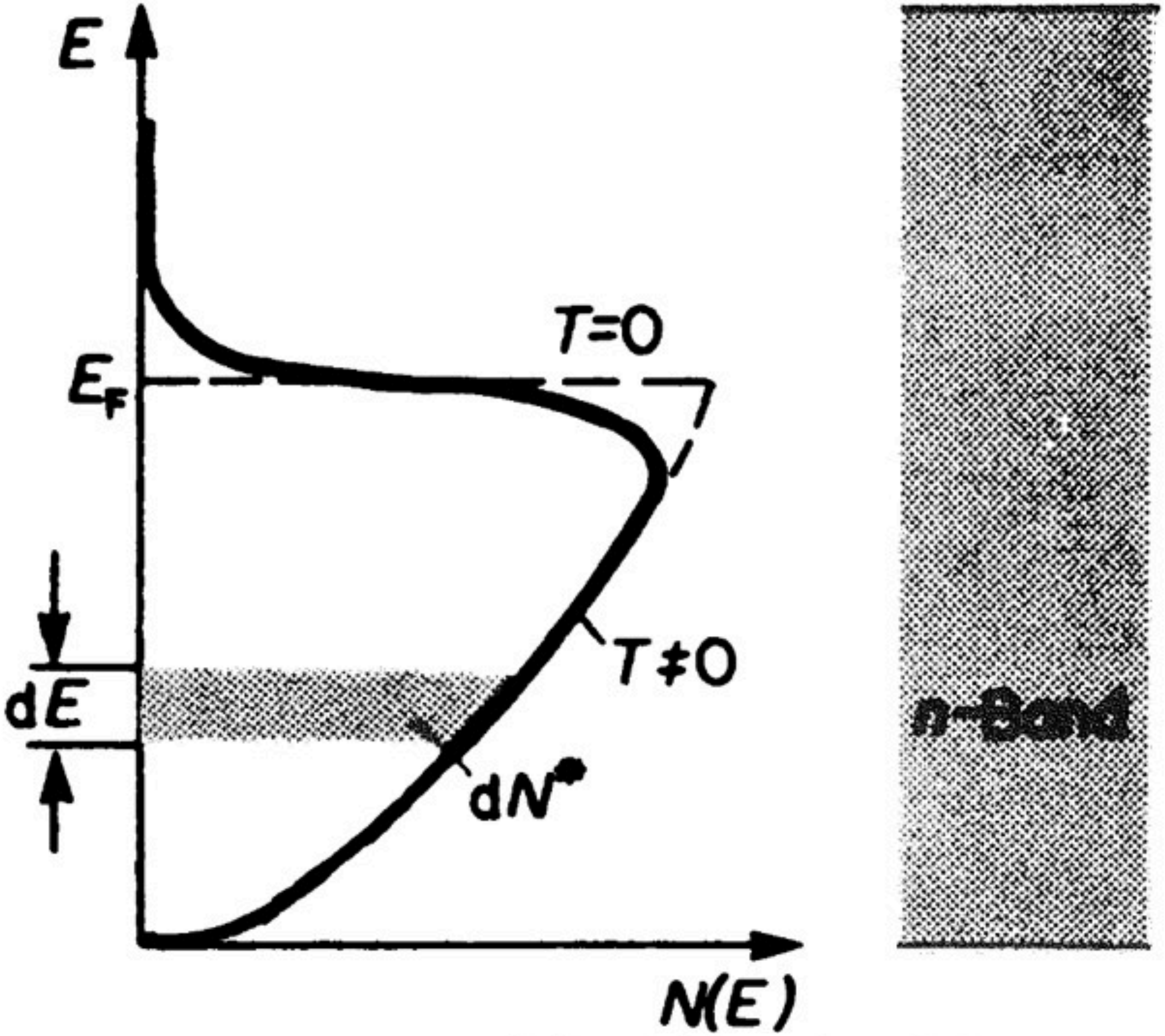
$$N(E) = 2 \cdot Z(E) \cdot F(E)$$

$$N(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}.$$

$N(E)$ is called the (electron) **population density**

$T \to 0$ and $E < E_F$, the function $N(E)$ equals $2 \cdot Z(E)$ because $F(E)$ is unity

$$N^* = \int_0^{E_F} N(E)\,dE = \int_0^{E_F} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}\,dE = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$



$$E_F = \left(3\pi^2 \frac{N^*}{V}\right)^{2/3} \frac{\hbar^2}{2m}$$

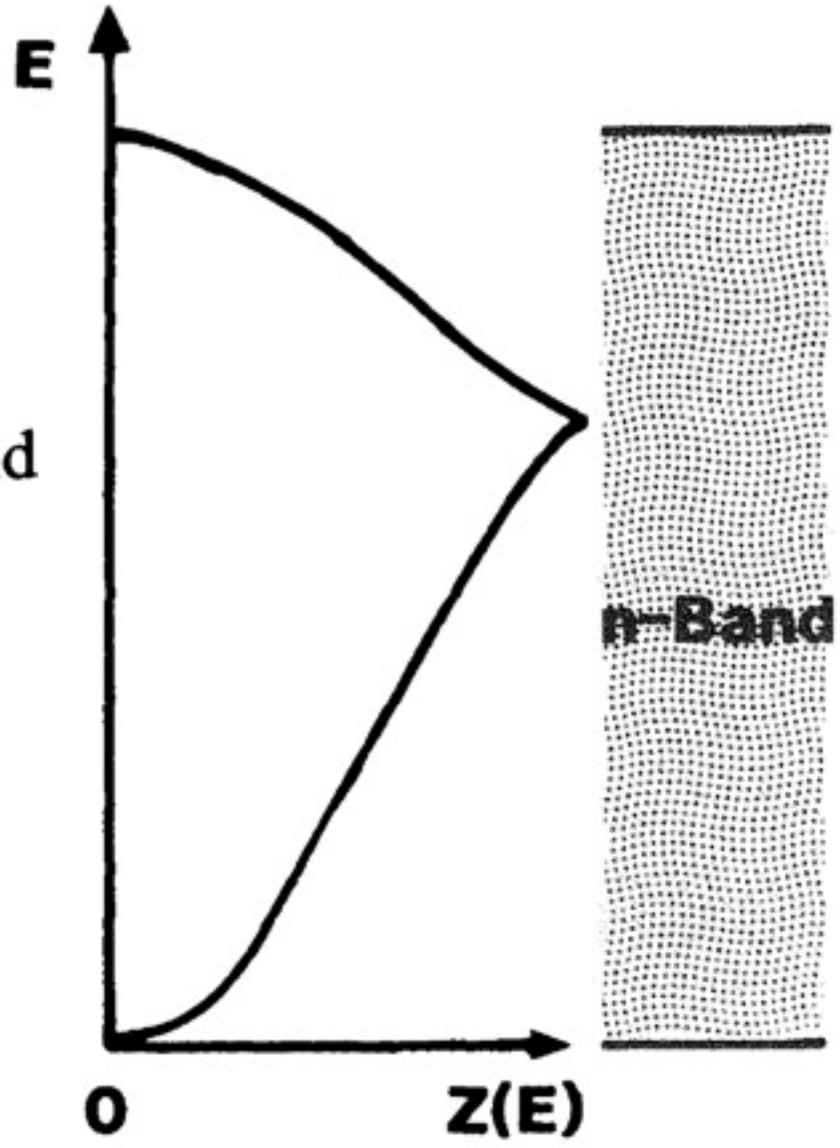
$$N(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1}$$

Population density $N(E)$ within a band for free electrons. dN^* is the number of electrons in the energy interval dE

6.5. Complete Density of States Function Within a Band (within a crystal)

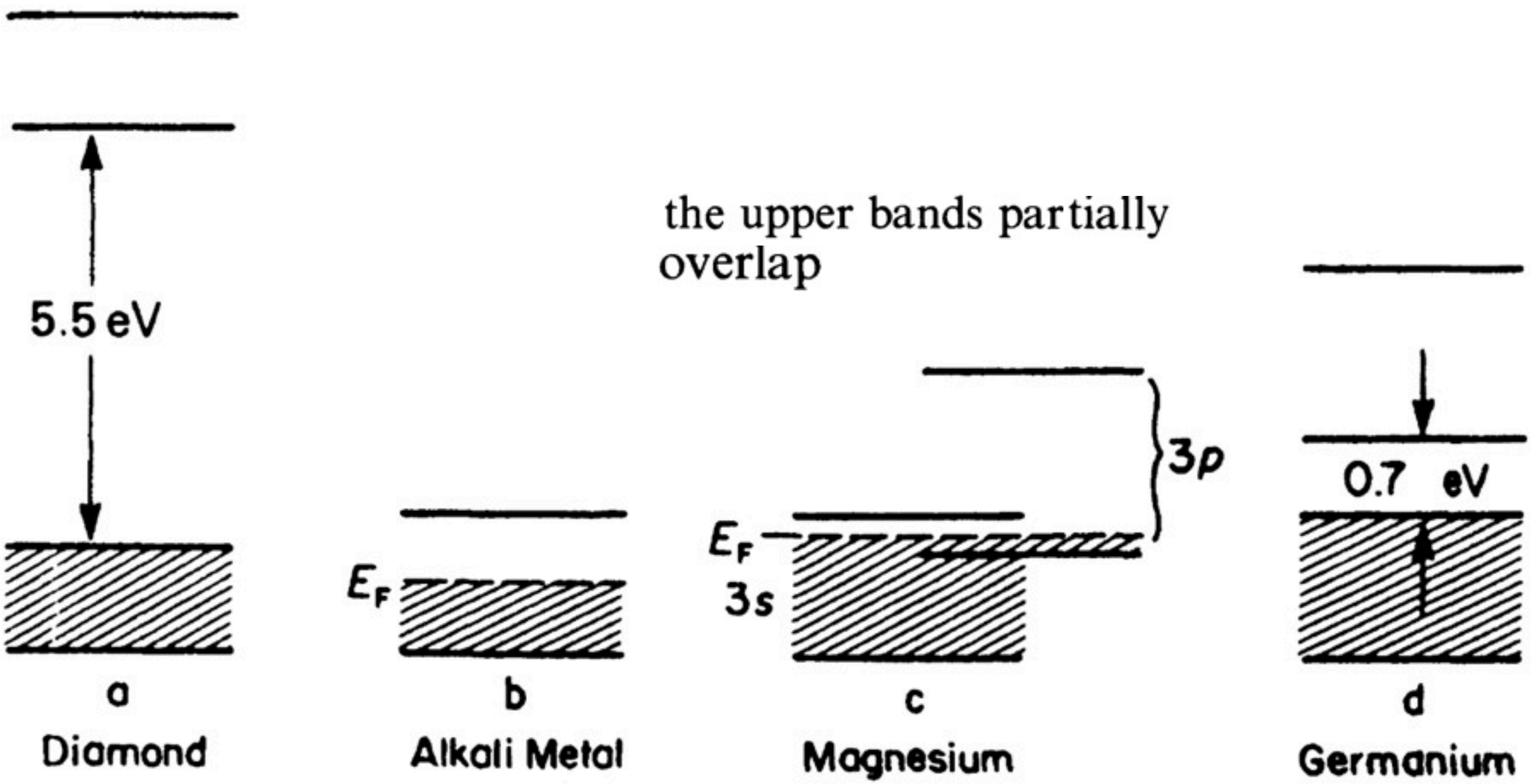
the density of states is modified by the energy conditions within the first Brillouin zone

The largest number of energy states is thus found near the center of a band



Schematic representation of the complete density of states function within a band

6.6. Consequences of the Band Model



the upper bands partially overlap

bivalent metals should be insulators

intrinsic semiconductors

small band gap

the highest filled band is completely occupied

the valence band is essentially half-filled

6.7. Effective Mass

velocity of an electron in an energy band

~ group velocity

$$v_g = \frac{d\omega}{dk} = \frac{d(2\pi\nu)}{dk} = \frac{d(2\pi E/h)}{dk} = \frac{1}{\hbar}\frac{dE}{dk}$$

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt}$$

$$\frac{dp}{dt} = \hbar\frac{dk}{dt}$$

$$a = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}\frac{dp}{dt} = \frac{1}{\hbar^2}\cdot\frac{d^2E}{dk^2}\cdot\frac{d(mv)}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}F$$

where F is the force on the electron

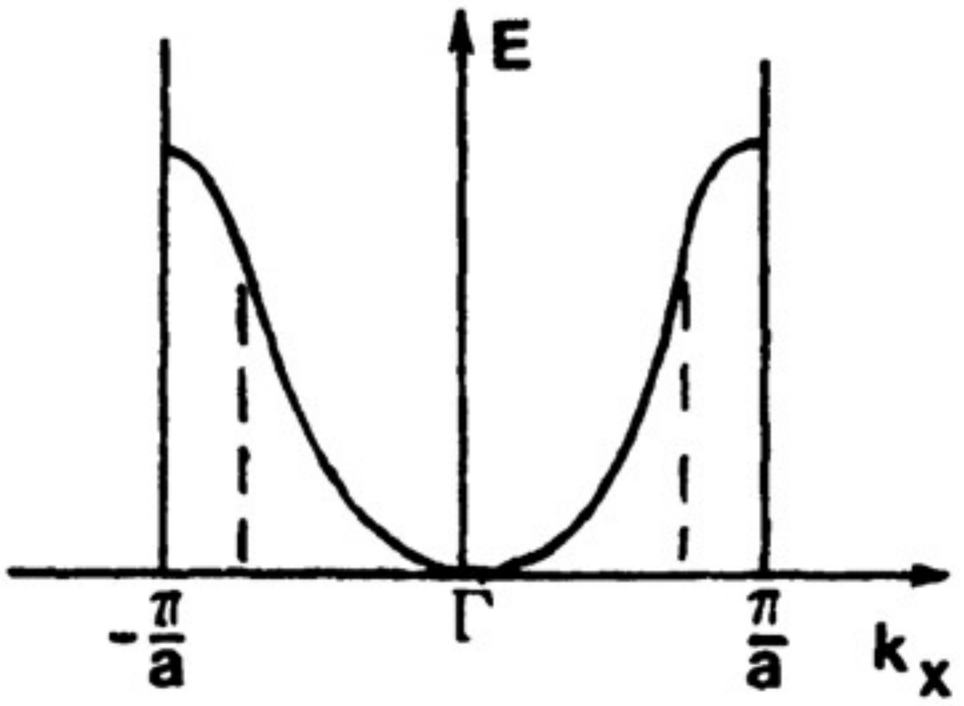
Newton's law

$$a = \frac{F}{m}$$

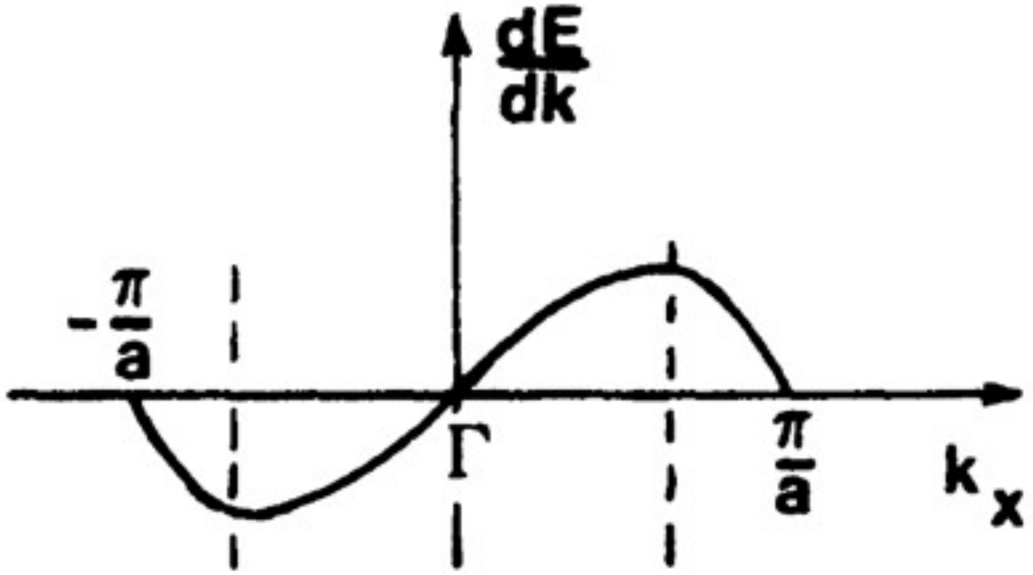
$$m^* = \hbar^2\left(\frac{d^2E}{dk^2}\right)^{-1}$$

the effective mass is inversely proportional to the curvature of an electron band

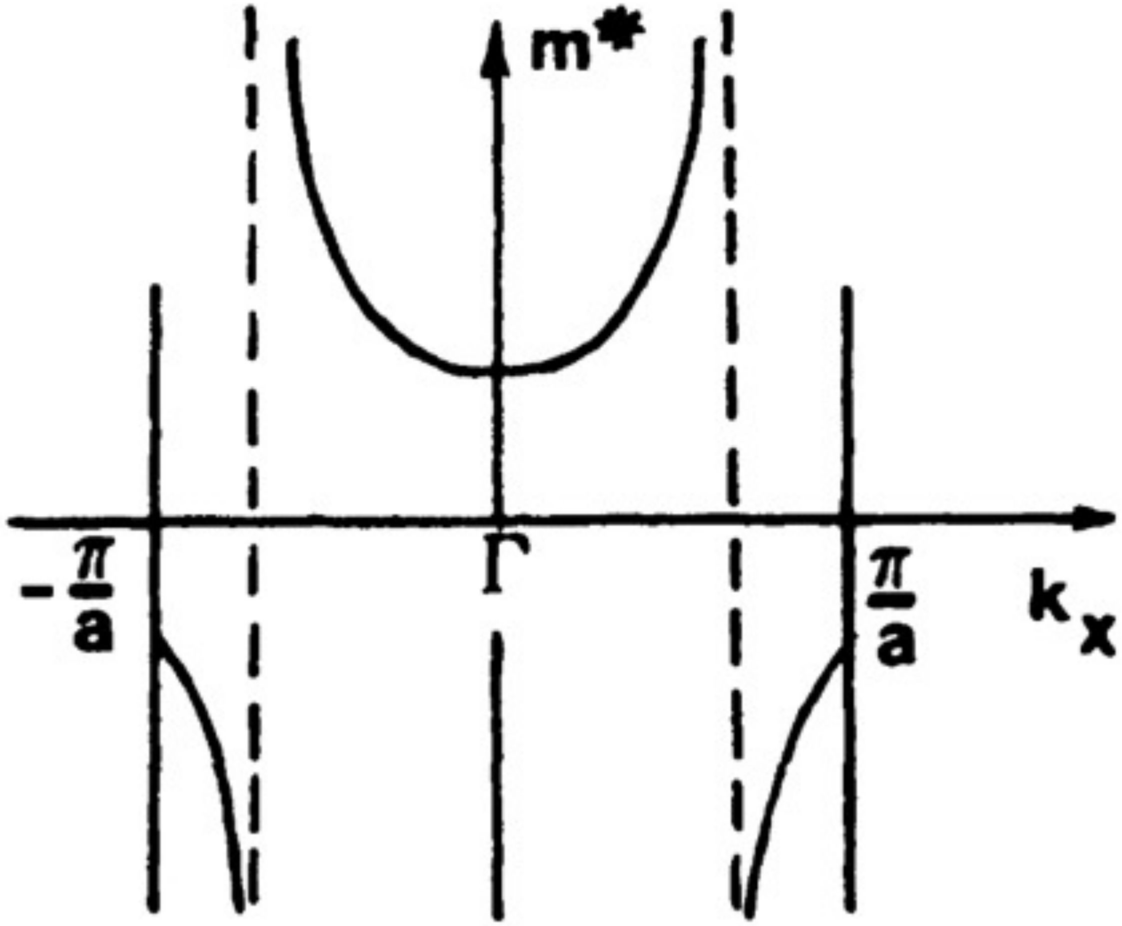
“electron hole.



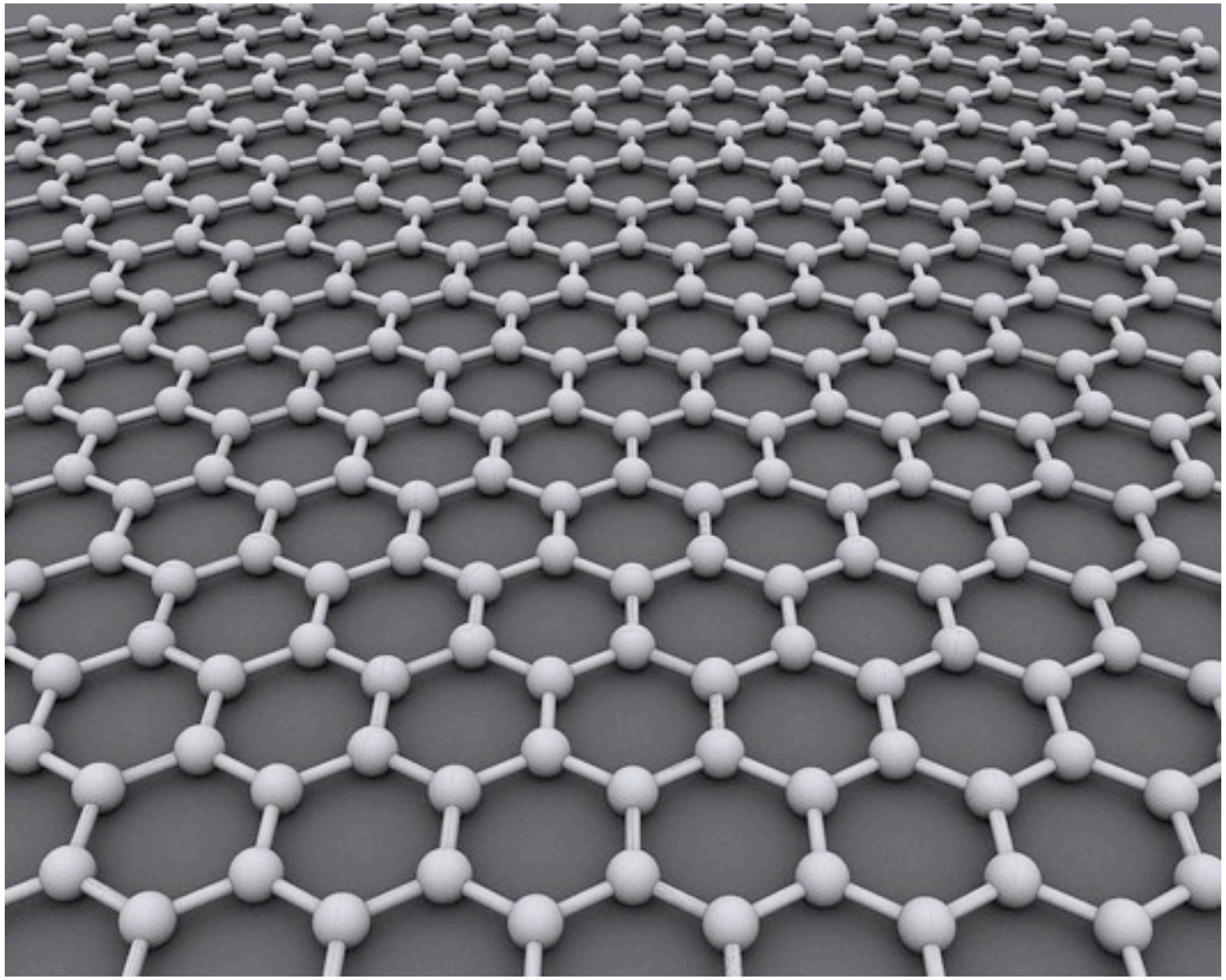
(a)

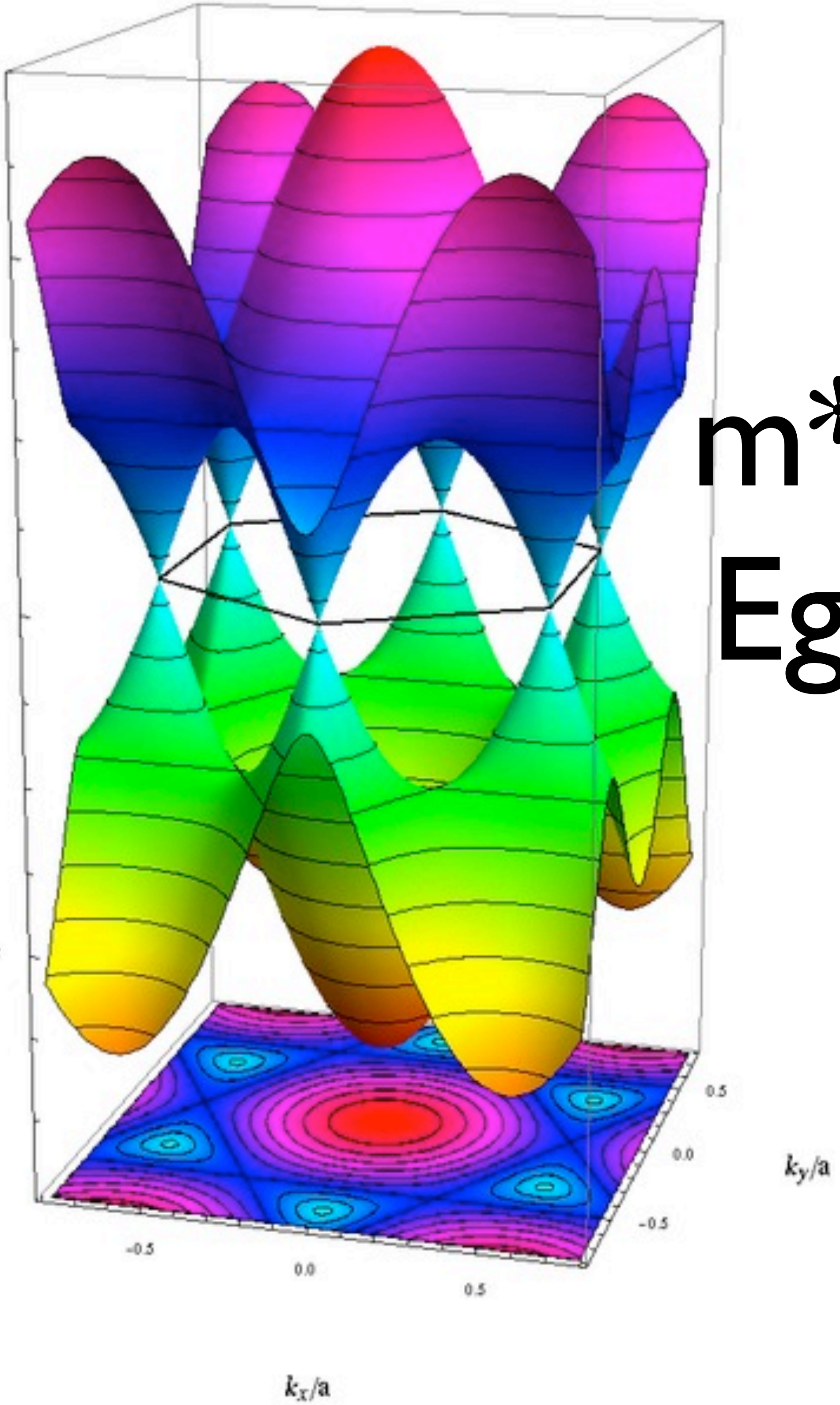


(b)



(c)





m*~0

Eg=0

Energy of the electrons with wavenumber **k** in graphene, calculated in the Tight Binding-approximation. The unoccupied (occupied) states, colored in blue-red (yellow-green), touch each other without energy gap exactly at the above-mentioned six k-vectors.