Free electron theory of metals

Density of Available Electronic states D(E)

By D(E) we mean the total number of available electronic states per unit energy range at E. This quantity is useful in the description of the behaviour of the free electron gas. To find the expression for D(E) we consider the linear momentum P which in the quantum mechanics is represented by operator

$$P = -i\hbar\nabla$$

Where as for the energy state,

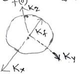
$$P\psi_k(r) = -i\hbar\nabla\psi_k(r) = \hbar k\psi_k(r) \qquad (1)$$

So that the plane wave ψ_k is an eigen function of the linear momentum with eigen value $\hbar k$. The particle velocity is given by

$$v = \frac{\hbar k}{m} \qquad (2)$$

In the ground state of a system of N free electrons the occupied orbitals may be represented as points inside a sphere in K-space. The energy at the surface of the sphere is the Fermi energy, the wave vectors at the Fermi surface have a magnitude K_f, such that

$$E_{f(0)} = \frac{\hbar^2 K_f^2}{2m} \qquad (3)$$



Here we see that there is one allowed wave vector for the volume element $\left(\frac{2\pi}{L}\right)^3$ of K-space. Thus in the sphere called Fermi sphere of volume $\frac{4}{3}\pi K_f^3$ the total number of orbitals is

$$\frac{2\times 4\pi K_f^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2}K_f^3 = N. \qquad (4)$$

when the factor 2 on the left comes from the two allowed values of m_s, the spin quantum number for each allowed value of K. We have put the number of orbitals equal to N, the number of electrons. from eqn (4) we have

$$K_f = \left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}} \quad \text{--- (5)}$$

This depends only on the particle concentration and not on the mass. Using eqn. (3) we have

$$E_{f(0)} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \quad \text{--- (6)}$$

This relates the fermi energy to the electron concentration $\frac{N}{V}$ and the mass m. The electron velocity v_f at fermi surface is

$$v_f = \frac{\hbar K_f}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{\frac{1}{3}} \quad \text{--- (7)}$$

The density of state function D(E) defined from the fact that all the energy states below $E_{f(0)}$ are occupied and this is equal to the total number of electrons i.e.

$$\int_0^{E_{f(0)}} D(E)\, dE = N \quad \text{--- (8)}$$

substituting the value of N from (5) we have

$$\int_0^{E_{f(0)}} D(E)\, dE = \frac{V}{3\pi^2}\left(\frac{2mE_{f(0)}}{\hbar^2}\right)^{3/2}$$

Expressing the integral as an indefinite integral we have,

$$\int D(E)\, dE = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

$$\text{or,} \quad D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{\frac{1}{3}} \quad \text{--- (9)}$$

$$= cE^{\frac{1}{2}}$$

$$\text{where} \quad c = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}$$

This result may be obtained and expressed most simply by writing eqn ⑥ as

$$\log N = \frac{3}{2} \log E_{f(0)} + \text{Const.}$$

or

$$\frac{dN}{N} = \frac{3}{2} \frac{dE_{f(0)}}{E_{f(0)}}$$

and we have

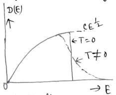
$$D(E_{f(0)}) = \frac{dN}{dE_{f(0)}} = \frac{3}{2} \frac{N}{E_{f(0)}} \qquad (10)$$

within a factor of the order of unity, the number of orbitals per unit energy range at the fermi-energy is just the total number of Conduction electrons devided by the fermi Energy.

These results apply to free electrons with energy (E) proportional to K^2. We can obtain a result for a general relation $E(K)$.

$$D(E) = \frac{2V}{(2\pi)^3} \int \frac{dS_E}{(\text{grad } E_K)} \qquad (11)$$

where the factor 2 arises from the two spin orientations. V is the volume of the specimen and ds is the element of area in k-space of the surface of Constant energy E.



It is seen from expression ⑨ that D(E) is a parabolic function of energy. This is plotted in above figure. Also it increases with increase in the crystal volume; this is inorder to accommodate the total number of electrons present which also increases with the size of the crystal.

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