

Table 9-4 Values of \mathcal{E}_F using Eq. 9-29a and the electron concentrations of the metallic elements from Table 9-1. Values of the equivalent Fermi temperatures, Fermi velocities and Fermi wave vectors are also given.

Element	\mathcal{E}_F (eV)	T_F (°K)	v_F (cm/sec)	k_F (cm ⁻¹)
Li	4.74	5.51×10^4	1.29×10^8	1.12×10^8
Na	3.24	3.77	1.07	0.92
K	2.12	2.46	0.86	0.75
Rb	1.85	2.15	0.81	0.70
Cs	1.59	1.84	0.75	0.65
Cu	7.00	8.16	1.57	1.36
Ag	5.49	6.38	1.39	1.20
Au	5.53	6.42	1.40	1.21
Be	14.3	16.6	2.25	1.94
Mg	7.08	8.23	1.58	1.36
Ca	4.69	5.44	1.28	1.11
Sr	3.93	4.57	1.18	1.02
Ba	3.64	4.23	1.13	0.98
Fe	11.1	13.0	1.98	1.71
Zn	9.47	11.0	1.83	1.58
Cd	7.47	8.68	1.62	1.40
Hg	7.13	8.29	1.58	1.37
Al	11.7	13.6	2.03	1.75
Ga	10.4	12.1	1.92	1.66
In	8.63	10.0	1.74	1.51
Tl	8.15	9.46	1.69	1.46
Sn	10.2	11.8	1.90	1.64
Pb	9.47	11.0	1.83	1.58
Bi	9.90	11.5	1.87	1.61
Sb	10.9	12.7	1.96	1.70

$T_F \gg 300^\circ\text{K}$. These large values of \mathcal{E}_F (and T_F) lead to Fermi velocities of the order of 10^8 cm/sec, which is much faster than thermal velocities. These large numbers come about because of the quantization of the free electron energy levels in the metal and because the Pauli principle restricts the number of electrons in each quantum state. Thus, the electrons fill much higher energy states than are required for a classical gas.

The wave vector – Via Eq. 9-27, \bar{m} and the wave vector \mathbf{k} are linearly related. Thus, just as in the case of \bar{m} -space, we may define \mathbf{k} -space or wave vector space. \mathbf{k} -space rather than \bar{m} -space will be used in Chapter 10 and Section 9-13. It is within \mathbf{k} -space that the Fermi surface is defined. Remember \bar{m} or \mathbf{k} are just *orbital quantum numbers*. We have already written the wave functions and energies in terms of \mathbf{k} in Eq. 9-26, and Fig. 9-4 showed the allowed states in \mathbf{k} -space. How-

ever, a change in labels from k_x and k_y to 9-4 appropriate to \bar{m} space as well. They realize. First, \mathbf{k} -space is uniformly filled corresponds to an allowed (quantum) state. In a sphere there are a huge number of allowed states. In a linear dimension the density is very large. In a linear dimension the number of allowed states is $\sim 1 \text{ cm}^{-1}$ (Eq. 9-27a). This on a scale that shows k_F , the allowed states form a continuum of \mathbf{k} -values.

Fermi surface – The Fermi surface is the boundary between the occupied and unoccupied states in \mathbf{k} -space. It is a surface of constant energy; in fact, for free electrons the Fermi surface is a sphere (or a sphere as we shall see in Chapter 10, for real metals it has a complicated shape. Although we define the Fermi surface, we shall see that \mathcal{E}_F hardly is affected by temperature. At high temperatures the surface remains sharp and the Fermi surface is very significant because it is only those states that are close to it that can participate in thermal excitations. These points are covered in Chapter 10. For the more complicated Fermi surfaces, in Chapter 10 these same general statements apply. The Fermi surfaces may vary but the physics is the same.

Density of states, $g(\mathcal{E})$ – This is defined as the number of states between \mathcal{E} and $\mathcal{E} + d\mathcal{E}$. To find $g(\mathcal{E})$, not $G(\mathcal{E})$, with energy up to arbitrary value of \mathcal{E} is

$$2 \left(\frac{4\pi}{3} \right) \bar{m}^3 = 2 \left(\frac{4\pi}{3} \right) \frac{V}{(2\pi)^3} k^3$$

where we have used Eqs. 9-26 and 9-27. The quantity is just

$$\int_0^{\mathcal{E}} g(\mathcal{E}) d\mathcal{E} = 2 \left(\frac{4\pi}{3} \right) \bar{m}^3 = \left(\frac{4\pi}{3} \right) \frac{V}{(2\pi)^3} k^3$$

so $g(\mathcal{E}) = (2^{1/2} V / \pi^2) (m/\hbar^2)^{3/2} \mathcal{E}^{1/2}$

where the constant C , defined by this equation, is of later convenience. Figure 9-5 shows a plot of $g(\mathcal{E})$ versus \mathcal{E} (and for $T > 0^\circ\text{K}$, which will be discussed later, the form is clear. At $T = 0^\circ\text{K}$ the states are shown. The parabolic form for $g(\mathcal{E})$ is not apparent in Fig. 9-5 because only the energy occupied states are shown.

Table 9-6 Measured and calculated (via Eq. 9-53) values of γ , the coefficient of the free electron term in the molar specific heat. The values are given in 10^{-4} calories moles $^{-1} \text{K}^{-2}$. (See Gopal for a more extensive list.)

Element	Meas.	Calc.	Element	Meas.	Calc.
Li	4.2	1.8	Fe	12	1.5
Na	3.5	2.6	Mn	40	1.5
K	4.7	4.0	Zn	1.4	1.8
Rb	5.8	4.6	Cd	1.7	2.3
Cs	7.7	5.3	Hg	5.0	2.4
Cu	1.6	1.2	Al	3.0	2.2
Ag	1.6	1.5	Ga	1.5	2.4
Au	1.6	1.5	In	4.3	2.9
Be	0.5	1.2	Tl	3.5	3.1
Mg	3.2	2.4	Sn	4.4	3.3
Ca	6.5	3.6	Pb	7.0	3.6
Sr	8.7	4.3	Bi	0.2	4.3
Ba	6.5	4.7	Sb	1.5	3.9

where we have used $g[\mathcal{E}_F(0)] = (3N/2)/\mathcal{E}_F(0) = (3N/2k_B)/T_F$ obtained from Eqs. 9-29 and 9-30b. The heat capacity per unit volume, $C_v = (\partial U/\partial T)_v$, is obtained directly from Eq. 9-52. However, the heat capacity per mole usually is measured. If we consider one mole of atoms and if each atom contributes Z electrons to the electron gas, then instead of $k_B N$ in Eq. 9-52 where N is the number of electrons, we write $Zk_B N_A = ZR$ where N_A is the number of atoms in a mole, which is Avogadro's number and R is the gas constant. Then the electronic heat capacity per mole is

$$C_v = (\pi^2/2)ZR [T/T_F] \equiv \gamma T \quad (9-53)$$

This is just the form expected as discussed qualitatively in Section 9-9. Instead of a value R , this is reduced to $R(T/T_F)$ because only the fraction (T/T_F) of the electrons, with energies near the Fermi energy, have empty states within a range $k_B T$ to which they can be excited.

Before we can compare the calculated electronic heat capacity to experimental values, the lattice heat capacity (Chapter 11) must be mentioned. For N harmonically coupled atoms, the classical energy is $3Nk_B T$, since for each atom there is $k_B T/2$ for each degree of freedom and there are three degrees of freedom for the kinetic energy and also three for potential energy. Then $C_v = 3Nk_B$, or $3R$, for a mole. However, since the atoms in a crystal are not classic but quantum mechanical, at low temperatures their energy and heat capacity are significantly different from the classical values. Low temperatures for a crystal lattice means temperatures low compared to the so called Debye temperature, which is typically several hundred degrees Kelvin!

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