Metal	$-\dfrac{d \ln \theta_R}{d \ln V}$	Grüneisen parameter γ	$\dfrac{d \ln K}{d \ln V}$
Li	1.0	0.9	− 3
Na	1.3	1.3	+ 1.8
K	1.4	1.3	+ 2.9
Cu	2.3	2.0	− 1.8

exclusion principle, however, this is not possible, since each state of kinetic energy can be occupied by only two electrons (of opposite spin). Consequently the electrons "fill up" all the lowest kinetic-energy levels available to them until all the electrons are accommodated. Therefore, at the absolute zero of temperature all the lower kinetic-energy levels are filled up to a certain value E_o, and above this the levels are all empty. The value of E_o in a typical monovalent metal, if expressed as an equivalent temperature, is around 50,000°K—in other words, this is the temperature to which a classical electron gas would have to be heated to have a similar kinetic energy. It is evident from this that even at room temperature the additional kinetic energy of the electrons that is due to thermal motion is tiny as compared to their zero-point energy, so that for some purposes we can treat the electrons as being effectively at 0°K. The maximum energy E_o of the electrons at 0°K (or more generally, their chemical potential) is referred to as the Fermi energy of the electrons, E_F, and this quantity varies with volume; in the simplest approximation of quasi-free electrons, $E_o \propto V^{-2/3}$.

How are the electron velocities distributed over the various directions in space? In an ideal gas the distribution would be isotropic—that is, the average velocity would be the same in all directions. In discussing electrons in metals it is more convenient to work, not directly with the electron velocity or momentum, but (since the properties of electrons are governed by wave mechanics) with the electron's wave number k, which in the case of completely free electrons would be related to the momentum by the De Broglie relationship $hk = p$. The energy of such electrons (of mass m) is given by $E = h^2 k^2 / 2m$, so if we plot the components of k, k_x, k_y, and k_z along cartesian axes (k-space), the surfaces of constant energy would therefore be spheres (corresponding to an isotropic distribution of velocities). The surface

corresponding to the Fermi energy of the electrons is called the Fermi surface. If the electrons are not free but are influenced by the potential field of the lattice, then the Fermi surface will no longer be a sphere but will be more or less distorted, depending on the influence of the lattice potential; the symmetry of the Fermi surface taken as a whole is closely related to that of the crystal. The importance of the Fermi surface arises from the fact that only electrons close to the Fermi surface have unoccupied electronic levels in their neighborhood—in other words, these are the only electrons which can be thermally excited (at normal temperatures) or scattered by lattice waves or impurities.

The wavelike properties of electrons imply that, like x-rays, electrons in a crystal may suffer Bragg reflections. Thus, if an electron propagating in a certain direction in the crystal has just the right wavelength to satisfy the Bragg condition, it will be reflected by the appropriate lattice planes. Suppose that we choose some particular direction in the crystal and then find the minimum value of k which an electron propagating in that direction must have to satisfy the Bragg relation; suppose, further, that we do this for all possible directions. Then if we draw these k-vectors from the origin in k-space, it turns out that their ends lie on a polyhedron about the origin, this polyhedron having the symmetry of the lattice. This polyhedron is referred to as the first Brillouin zone of that lattice, and it is relevant to any kind of wave that can propagate through the lattice (in particular lattice waves and electrons). If for the electrons we draw surfaces of constant energy in k-space, all those surfaces lying within the Brillouin zone are continuous, whereas those surfaces which intersect the zone boundary will, in general, suffer a dis-
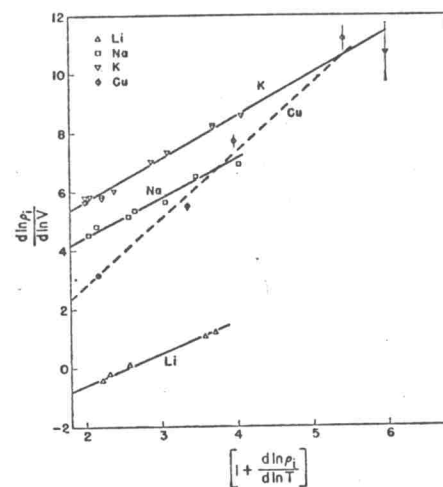

Fig. 5. The logarithmic volume coefficient of the ideal resistivity of lithium, sodium, potassium, and copper, shown as a function of the logarithmic temperature coefficient.

continuity; there is in fact a forbidden energy region at the zone boundaries such that electrons with energies lying within this range cannot propagate in the lattice.

The volume of the zone in k-space is such that if the crystal has N atoms per unit volume (15), then the zone can accommodate N electrons of a given spin, uniformly distributed throughout the zone. Since electrons can exist in two independent spin states of the same wave vector, the zone can contain just $2N$ electron states.

This latter conclusion has the following important consequence. In a monovalent metal, which has just one conduction electron per atom, the Fermi surface which encloses all the electron states in k-space must therefore comprise a volume equal to half that of the Brillouin zone. This in turn means that if in cubic monovalent metals the Fermi surface is nearly spherical it can be entirely contained within the first zone without anywhere touching it. This

Table 2. Data on resistivity for the monovalent metals.

Metal	$\dfrac{d \ln \rho_i}{d \ln V}$ at 0°C	2γ	$\dfrac{d \ln K}{d \ln V}$	$\left(\dfrac{d \ln \rho}{d \ln E}\right)_V \equiv x$	$\dfrac{d \ln K}{d \ln V} \Big/ x$	θ_o	θ_R*	θ_R/θ_o	$\dfrac{M\theta_o^2 V^{1/3}\rho_i}{T}$
Li	−0.49	1.8	−2.3	6.7	−0.3	369†	385†	1.04	7.2
Na	4.6	2.6	2.0	−2.7	−0.7	152‡	205‡	1.35	2.0
K	5.7	2.6	3.1	−3.8	−0.8	90	116	1.29	2.0
Rb	3.7	3.0	0.7	−2.3	−0.3	55	58	1.06	3.1
Cs	(4)	3.2		−0.2		40	45	1.13	4.4
Cu	3.0	4.0	−1.0	+1.6	−0.6	344	333	0.97	8.4
Ag	3.9	4.8	−0.9	+1.1	−0.8	225	223	0.99	6.3
Au	5.5	6.2	−0.7	+1.5	−0.5	165	175	1.06	13.5

* The value for cesium was taken from MacDonald (1). The other values of θ_R were taken from (13) and (9) for the alkali metals and from (27) for the noble metals. † Two-phase mixture.
‡ Estimated value for the body-centered cubic phase.