In contrast, sodium and potassium are thought, from theoretical calculations and from a consideration of their transport properties, to have almost spherical Fermi surfaces (see, for example, Ham 1960; Cohen & Heine 1958). For these metals $\mathrm{d}\ln K/\mathrm{d}\ln V$ is about $+2$, and this implies that as the volume is decreased so the interaction between the electrons and the phonons decreases. This seems quite reasonable because one would expect *a priori* that as the electrons at the Fermi surface become more energetic, so their scattering for a given amplitude of vibration of the lattice would diminish.

According to the calculations of Ham (1960), the Fermi surfaces of all the alkali metals except sodium become more distorted under pressure. In sodium (according to these calculations) the Fermi surface remains effectively spherical up to moderate pressures but at higher pressures it too begins to become distorted. It is tempting to ascribe the minima that have been found by Bridgman in the resistance–pressure curves of the alkali metals at room temperature to a progressive distortion of the Fermi surface under pressure (cf. Dugdale 1961). In lithium the distortion of the Fermi surface is already large enough to make the resistance increase with pressure even at the lowest pressures; for the other alkali metals the increase of distortion with pressure (predicted by Ham) is, on this hypothesis, ultimately sufficient to cause the resistance of these metals also to increase with pressure (cf. also Frank 1935).

4·2·4. *The correlation of* $\mathrm{d}\ln K/\mathrm{d}\ln V$ *with the thermoelectric power*

The thermoelectric power of a metal at high temperatures ($T > \theta$) may be related to the energy dependence of electrical resistivity by the expression (which neglects phonon drag)

$$S = -\frac{\pi^2 k^2 T}{3e}\left(\frac{\partial \ln \rho(E)}{\partial E}\right)_{E=E_F}. \tag{6}$$

Here $\rho(E)$ is the electrical resistivity of the metal for electrons of energy E and the derivative is to be evaluated at the Fermi level; e is the electronic charge and k is Boltzmann's constant. The significance of this expression is discussed by Ziman (1960). Equation (6) may be rewritten in the form

$$S = -\frac{\pi^2 k^2 T}{3eE_F}\left(\frac{\partial \ln \rho(E)}{\partial \ln E}\right)_{E=E_F}, \tag{6A}$$

where we have now introduced E_F, the Fermi energy measured from the bottom of the conduction band. From this expression and the measured values of S at high temperatures it is then possible to evaluate the quantity $(\partial \ln \rho(E)/\partial \ln E)_{E_F}$ (which for brevity we shall call x) for the monovalent metals†. This quantity x which measures the change in resistivity of the metal as the Fermi energy alters might be expected to be related in some way to the volume coefficient of electrical resistivity (cf. Friedel 1956). MacDonald & Pearson (1953) compared x directly with the logarithmic volume derivative of the electrical resistivity for the alkali metals and established that some correlation existed. It would seem, however, more appropriate to compare values of $\mathrm{d}\ln K/\mathrm{d}\ln V$ with the corresponding values of x, since in

† In doing this we shall use the free electron value for E_F.