the term in the $\langle \quad \rangle$ is positive, and the contribution to the thermopower is negative. For an umklapp process, where $\vec{K}$ is not 0, $\vec{s}$ can be anti-parallel to $\vec{q}$ and the contribution to the thermopower positive. In an extended zone scheme, the size of the smallest phonon wave vector with which an umklapp process may occur is determined by the shortest distance between adjacent Fermi surfaces and changes if the surfaces are warped. Ziman calculated the temperature dependence of the thermopower for various amounts of bulging of the Fermi surface and found he could fit the experimental data for sodium and potassium quite well. The rubidium and cesium data were not fitted in detail. For lithium, the thermopower is positive throughout the temperature range; this is taken to suggest that the Fermi surface actually touches the zone boundary. Ziman concludes that in sodium the surface is nearly spherical, and that the anisotropy increases as we go through the series potassium, rubidium, cesium and lithium.

Ziman's calculation is a rough one; he does not take the large anisotropy of the velocity of sound in alkalis into account and this could well change the size of the warping he obtains. However, we do expect that the differences between the various alkalis should show up in this calculation. In a more recent paper Bailyn suggests that differences in the anisotropy of the transverse phonon spectrum for the various alkalis may also be able to explain the observed thermopowers and that the relative importance of these two proposed causes is not at all clear [42].

We have seen that both the magneto-resistance data and the thermopower data have been used to infer that lithium is the alkali metal with the most anisotropic Fermi surface; the surface may even touch the zone face. Cohen and Heine [43] have inferred touching of the surface in lithium from the pressure dependence of the resistance. In all the alkali metals except lithium, the resistance initially decreases as pressure increases. The conductivity may be written as

$$\sigma = \frac{e^2}{4\pi^3 \hbar} \int v\,\tau(\vec{k})\, dA \propto \overline{v}\,\overline{\tau}\,A \qquad (I\text{-}8)$$

where the integral is taken over the Fermi surface, v is the electron velocity, $\tau(\vec{k})$ is the scattering time at point $\vec{k}$, d A is an element of area on the Fermi

surface, $\bar{v}$ and $\bar{\tau}$ are average velocities and scattering times and A is the area of the Fermi surface. The usual explanation of the effect of pressure on the conductivity is that increasing pressure decreases the amplitude of the lattice vibrations, increasing τ [44]. Cohen and Heine proposed that the effect in lithium is dominated by the increase of the area of contact with pressure; this can decrease the area of the Fermi surface and increase the resistivity. According to Bailyn [45] increased contact creates a narrower shape for the Fermi surface, with smaller cross sections; this decreases the velocities on the surface and increases the resistivity. Cohen and Heine also claim that the increased contact enhances scattering by umklapp processes and opposes the effect of the lattice vibrations on τ. We have been able to draw Fermi surfaces in which increased contact increases the area of the Fermi surface. An example is the case where the unoccupied region of k space is spherical. Since the volume of this unoccupied region must stay constant and a sphere encloses this volume with the smallest possible surface area, any increased contact increases the area of the Fermi surface. This example points out that statements about the effect of touching should be accompanied by some picture of the original shape of the Fermi surface; without this, arguments on the effect of touching are not convincing.

Brooks [46] has pointed out that the decrease of the conductivity of lithium with pressure can be explained without invoking touching of the Fermi surface with the zone boundary. Calculations of the effective mass, such as those made by Brooks using the quantum defect method and summarized by Ham [47] show that m^* increases as the pressure increases. Since

$$v \propto dE/dk \propto 1/m^* \qquad \text{(I-9)}$$

the average velocity $\bar{v}$ will decrease with pressure. Likewise the decrease in the density of states factor $|\nabla_k E|$ in the expression for τ (see Sec. IV, Eq. IV-37) lowers τ.

The fact that the K X-ray emission for lithium does not drop sharply in intensity at the high energy end of the band has been used to infer strong deviations from free electron behavior [48]; this may indicate actual touching of Fermi surface with the zone boundary.