

higher densities for each metal. There is thus *no* anomalous behaviour in the high temperature resistivity of rubidium as described by MacDonald (1952). The effects that he found can almost certainly be ascribed to capillary constraints in his specimens.

Bailyn (1960) has calculated the temperature dependence of the resistivity of all the alkali metals. He found reasonable agreement with experiment for caesium and poor agreement for the others. (For lithium the agreement was good but, as already mentioned, the model used was not strictly appropriate to this metal.) Bailyn was inclined to attribute this poor agreement to the phonon spectra he used. The values he adopted for the anisotropy parameters are shown in table 11, together with the experimental values where these are known. It seems that his values of the anisotropy for sodium and potassium were indeed too large and this may account for much of the discrepancy. The more recent calculations of Bross & Holz (1963) and of Hasegawa (1964) used the neutron data on sodium and the specific heats as a check on their calculated dispersion relations. They then found reasonably good agreement with experiment for the temperature dependence of the resistivity of sodium, potassium and lithium. (For lithium the fact that the Fermi surface is not spherical had to be taken into account.)

Working more directly from the neutron data, Darby & March (1964) also found reasonable agreement for sodium. Still more recently Greene & Kohn (1965) have calculated the temperature dependence of the resistivity of sodium using the neutron data directly to give information about the motion of the ions. They have made what are probably the most refined calculations so far and find some disagreement with experiment. They discuss whether the discrepancy could be due to non-equilibrium of the phonons, although they think this unlikely. By comparing their results with those of Darby & March they conclude that anharmonic effects are important, in particular the change in elastic constants with temperature, and when they take this into account they find agreement with experiment within an accuracy of about $\pm 20\%$.

It seems therefore that although the agreement for sodium is not as complete as might have been expected these calculations are generally speaking successful. We may therefore expect that when we know the phonon dispersion curves for rubidium and caesium it will then be possible to calculate successfully the temperature dependence of their resistivities.

4.4. *How the resistivity depends on pressure*

At high temperatures ($T > \theta_0$) we may think of the resistivity as proportional to the square of the amplitude of the lattice vibrations and write for the ideal resistivity ρ_i at temperature T

$$\rho_i = KT/M\theta^2, \quad (1)$$

where M is the mass of the ions, θ is the characteristic temperature of the lattice and K represents all the factors associated with the interaction of the electrons with the lattice waves. We may then write

$$\left(\frac{\partial \ln \rho_i}{\partial \ln V}\right)_T = 2\gamma_G + \frac{d \ln K}{d \ln V}.$$

In this we have assumed that the changes in the amplitude of the lattice vibrations can be taken account of through the Grüneisen parameter γ_G . In table 14 we have listed the values of $d \ln K/d \ln V$ calculated in this way. γ_G has been evaluated from the thermal expansion, compressibility and specific heat of the solid. For rubidium and caesium some of these data are rather uncertain.

At low temperatures the ideal resistivity varies more strongly with temperature than at high temperatures (approximately as T^5 at the lowest temperatures). This means in effect that ρ_i depends more strongly on the amplitude of the lattice vibrations at low temperatures than at high. We may therefore expect that this will also show up in the *pressure* dependence of ρ_i (since pressure also changes the amplitude of the lattice vibrations) and that the pressure coefficient of ρ_i will

TABLE 14

metal	$\frac{\partial \ln \rho_i}{\partial p}$	$-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$	$\frac{\partial \ln \rho_i}{\partial \ln V}$	$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$	γ_G^*	$\frac{d \ln K}{d \ln V}$	$\frac{d \ln K \dagger}{d \ln V}$
	0°C (10^{-5} atm^{-1})	0°C (10^{-5} atm^{-1})	0°C	0°C ($10^{-5} \text{ per } ^\circ\text{C}$)		(expt.)	(theory)
lithium							
$p = 0$	+0.43	0.87 ₅	-0.49	14	0.9 ₀	{-2.3}	-3.7
$V = V_0$	—	—	—	—			
sodium							
$p = 0$	-7.3	1.58	4.6	21	1.3	{2.0}	1.8
$V = V_0$	-6.2	1.40	4.4 ₆	—			
potassium							
$p = 0$	-19.1	3.43	5.6	25	1.3	{3.0}	1.9
$V = V_0$	-15.8	2.82	5.6	—			
rubidium							
$p = 0$	-21	5.0	4.3	24	1.0	{2.3}	—
$V = V_0$	-17	3.6	4.7	—			
caesium							
$p = 0$	-22	7.1	3.1	29	1.0	{1.1}	—
$V = V_0$	-14	4.4	3.2	—			

* The data are not available to calculate γ_G at $V = V_0$ so we have assumed that the values at $p = 0$ and at $V = V_0$ are the same.

† Hasegawa (1964).

become more negative at low temperatures. This effect can be seen in figure 6 which shows how the pressure coefficient of ideal resistivity (at constant density) varies with temperature for all the alkali metals. (The data for lithium, sodium and potassium are taken from I.) As already stressed, the very low temperature values tend to be uncertain because of departures from Matthiessen's rule. Nevertheless, the tendency to become more negative at low temperatures in rubidium and caesium (as in the other metals) is clearly evident and qualitatively reliable. At higher temperatures the coefficient tends to be constant; the changes near room temperature may be real or they may be only a consequence of using slightly wrong data for the equation of state.

To show how the resistivity of the alkali metals varies with pressure over a wider pressure range, we show in figure 7 the relative resistivity ρ/ρ_0 as a