

where $\gamma_R (= -d \ln \theta_R / d \ln V)$ is a parameter which is analogous to the Grüneisen parameter, γ_G . The Grüneisen parameter is defined as follows:

$$\gamma_G \equiv -d \ln \theta_D / d \ln V = V \alpha / C_v \beta, \quad (4)$$

where θ_D is the Debye temperature, α the volume expansion coefficient, β the compressibility, C_v the atomic heat at constant volume, and V the atomic volume.

On the not unreasonable assumption that $\gamma_R = \gamma_G$ it is possible to estimate values of $d \ln K / d \ln V$ from high temperature measurements alone and it is interesting to compare the values so deduced with those calculated theoretically. Lawson (1956) has made such a comparison with the predictions of several different theoretical models of a metal and in his notation we have

$$\frac{d \ln K}{d \ln V} = 1 + 2 \frac{d \ln C}{d \ln V} + 2 \frac{d \ln m^*}{d \ln V}, \quad (5)$$

where C is a coupling energy (different in the different models) of the same order as the Fermi energy, and m^* is the effective mass of the conduction electrons. The last term in equation (5), i.e. the variation of the effective mass with volume, has been calculated for the alkali metals by Brooks (1953) (see also Ham 1955), and it turns out to be negligible for sodium and potassium but quite large for lithium for which $d \ln m^* / d \ln V$ is -0.8 . Apart from the last term in equation (5), $d \ln K / d \ln V$ has been variously calculated for free electrons as -1 (Seitz 1940), $-\frac{1}{3}$ (Peterson & Nordheim 1937), both for the 'deformable ion' model, and -1 (Lenssen & Michels 1935) for the 'rigid ion' model. Using the 'tight binding' approximation, Lenssen & Michels obtained a value of $+1$.

The free-electron approximation is expected to hold rather well for sodium and potassium, much less well for lithium and copper (cf. Cohen & Heine 1958). It is therefore surprising to see from table 13 that the experimental values of $d \ln K / d \ln V$ for sodium and potassium (about $+2$) are quite different from the predicted values of -1 or $-\frac{1}{3}$. On the other hand, the agreement is better for lithium and copper, although certainly in copper and probably in lithium the Fermi surface is considerably distorted from the free electron sphere. It is thus evident that the present theory of the change of resistivity with volume is inadequate (at least for high temperatures), since it fails for those metals (sodium and potassium) for which it should be most successful.

This inadequacy in the theory of the volume dependence of electrical resistivity raises the question as to whether the assumption that $\gamma_R = \gamma_G$ is a sound one. Returning to equation (2), we see that, since both $d \ln K / d \ln V$ and $d \ln \theta_R / d \ln V$ are assumed to be independent of temperature, then $\partial \ln \rho_i / \partial \ln V$ should be linearly related to $\partial \ln \rho_i / \partial \ln T$. One purpose of these experiments was to find out whether this relation is valid. If it holds, it might then be possible to deduce separately the values of $d \ln K / d \ln V$ and $d \ln \theta_R / d \ln V$ and so test directly whether θ_R changes with volume in the same way as θ_D . In short, if equation (2) is valid, we may hope to find out how much of the pressure coefficient of resistivity derives from changes in the lattice properties of the metal and how much from changes in the properties of the conduction electrons.