We will base our analysis on Ziman's [2] well known solution of the transport problem obtained with a variational method:

$$\varrho = \frac{3\pi\hbar}{2e^2 M N k T S^2 k_F^2} \sum_\lambda \iint \frac{q^2 (e_{\lambda,q} \cdot q)^2 \mathscr{V}^2(|q|)}{[e^{\hbar\omega_{\lambda,q}/kT}-1][1-e^{\hbar\omega_{\lambda,q}/kT}]} \frac{dS}{v} \frac{dS'}{v'} \tag{1}$$

$q = k - k'$. The integration dS extends over the Fermi surface, whose free area is S. Phonons of branch λ and wavevector q have frequencies $\omega_\lambda(q)$ and polarization vectors e_λ. The electron-phonon interaction has been approximated by the form factor $\mathscr{V}(|q|)$ that only depends on the magnitude of the momentum transfer $q = k - k'$. M is the ion mass, N the number of unit cells per unit volume and v and v' the velocities of an electron at the Fermi surface. The rest of the quantities have their usual meaning. An earlier calculation of resistivities for some polyvalent metals [3] with the use of Eq. (1) was in good agreement with experiments and the results obtained in this paper are also reasonable, so we believe that Eq. (1) is accurate enough in this context. It is interesting to note that we could in principle make a selfconsistent treatment, if we knew how the pseudo-potential changed with pressure. Once we had this information we could calculate changes in the phonon frequencies, the shape of the Fermi surface and the density of states of the conduction electrons, but such a procedure would not only be very difficult but also in practice give inaccurate results. Instead we shall use all available information to see how different parts in Eq. (1) contribute to a change in ϱ. For a discussion of the volume dependence it is very convenient to consider $(d \ln\varrho/d \ln V)$ and we write

$$\frac{d\ln\varrho}{d\ln V} = \frac{2 d\ln m_b}{d\ln V} - \frac{2 d\ln\Theta_R}{d\ln V} + \frac{d\ln I_R}{d\ln V} + 1. \tag{2}$$

The first term on the right hand side of Eq. (2) comes from the volume dependence of the band density of states at the Fermi level, i.e. essentially from dS/v, and we have taken an average over the Fermi surface in the form of an effective mass. We will always consider the resistivity at high temperatures (i.e. $T \gg \Theta_D$) and then the phonon frequencies come in as $1/\omega_\lambda^2(q)$ in the integrand of Eq. (1). This leads to the term

$$- 2(d\ln\Theta_R/d\ln V).$$

The phonon spectrum is differently weighted in different properties like e.g. the electrical resistivity and the vibrational specific heat. The relative frequency shift is not the same for all phonons and we must therefore be careful to specify which experiment we are considering. This is why we use the notation Θ_R and it does not imply the use of a Debye model or any other model. $(d \ln I_R/d \ln V)$ contains the effect of a variation in the form factor $\mathscr{V}(q)$. Finally there remain some terms that we assume to vary linearly with the lattice dimension and this gives $+1$ in the right hand side of Eq. (2). We shall later consider volume changes caused by external pressure and by the thermal expansion so we do not yet specify whether the temperature or the pressure is to be kept constant in the derivatives in Eq. (2).

The thermal expansion coefficient β can be written

$$\beta/K_T = \left(\frac{\partial S}{\partial V}\right)_T \tag{3}$$

where K_T is the isothermal compressibility and S the entropy. At low temperatures the thermal expansion of a non-magnetic metal consists of one contribution from the conduction electrons, which is linear in T, and one phonon contribution which goes like T^3. The entropy of the electrons is proportional to the total effective electron mass and it is evident from Eq. (3) that a measurement of the low temperature thermal expansion can give information about the volume dependence of the effective mass. A review of this method has been given by Collins and White [4]. A measurement of the pressure dependence of the critical field of a superconductor can in principle give the same information about the mass. At present this latter type of experiment seems to be less accurate than the first method [5]. In both cases the change in the *total* effective mass m_{eff} is obtained. If we neglect the influence of electron-electron interaction, we can write

$$m_{eff} = m_b(1 + \lambda) \tag{4}$$

where $1 + \lambda$ is the factor by which the band mass m_b is increased due to electron-phonon interaction. For λ we can write [6]

$$\lambda = \frac{1}{(2\pi)^3 M N \hbar} \sum_\lambda \iint \frac{(e_{\lambda,q} \cdot q)^2}{\omega^2(q)} \mathscr{V}(|q|) \frac{dS}{v} \frac{dS'}{v'} \Big/ \int \frac{dS}{v}. \tag{5}$$

Therefore, in analogy with Eq. (2)

$$\frac{d\ln m_{eff}}{d\ln V} = \frac{d\ln m_b}{d\ln V} + \frac{\lambda}{1+\lambda} \frac{d\ln\lambda}{d\ln V} \tag{6}$$

where

$$\frac{d\ln\lambda}{d\ln V} = \frac{d\ln m_b}{d\ln V} - \frac{2 d\ln\Theta_\lambda}{d\ln V} + \frac{d\ln I_\lambda}{d\ln V}. \tag{7}$$

Like in Eq. (2) the term $- 2(d \ln\Theta_\lambda/d \ln V)$ is the effect of shifts in the phonon frequencies but now they are averaged according to Eq. (5). The last term, $(d \ln I_\lambda/d \ln V)$, is the result of a change in $\mathscr{V}(q)$ in Eq. (5). The derivatives in Eq. (6) are to be taken at constant temperature (cf. Eq. (3)). There is no a priori reason why the various band masses we have introduced should have the same volume dependence, as they correspond to different averages over the Fermi surface. However, we do not expect them to behave in a very different way, and moreover this point is not crucial for any of the conclusions in this paper.

Pressure Dependence of the Resistivity

The resistance of various metals under pressure has been measured by Bridgman [7]. After taking into account that we want resistivity instead of resistance, we have at room temperature and in the limit of small volume changes $(d \ln\varrho/d \ln V)_T = 6.9$. Fisher [8] obtained the value 6.5, but Bridgman considers his experimental method to be somewhat uncertain. Throughout this paper we will use the compressibility and thermal expansion coefficient given by Gschneider [9] to convert from experimentally determined pressure or temperature derivatives to the corresponding volume derivatives.

The phonon term, $(d \ln\Theta_R/d \ln V)_T$, could in principle be obtained from measurements of phonon frequencies in lead under pressure. The experimental