uncertainties are, however, very large, and we defer a closer discussion of this experiment to the later comparison between effects of an external pressure and of thermal expansion. The standard approach in the literature has been to take $(d \ln \Theta_R/d \ln V)_T$ equal to the well known Grüneisen constant, γ_G, without any further justification. In appendices 1 and 2 we show that the use of γ_G is a reasonable approximation for lead.

The term $(d \ln I_R/d \ln V)$ is very difficult to discuss accurately. In order to make any further progress possible, we already in Eq. (1) made the approximation with a form factor $\mathscr{V}(q)$ which only depends on the magnitude of the momentum transfer. In a polyvalent metal this leads to erroneous results for those scattering processes where $\boldsymbol{k}$ and $\boldsymbol{k}'$ differ by a reciprocal wave vector [10]. On the other hand, recent calculations by CARBOTTE and DYNES [11], using the form factor for all scattering processes, has given quite good results for both lead and aluminium, indicating that this approximation could give a good over all description. There are recent measurements of the de Haas-van Alphen effect in lead under pressure [14]. From this experiment, the two derivatives $d\mathscr{V}_{111}/dp$ and $d\mathscr{V}_{200}/dp$ of the form factor can be deduced. It turns out that a simple model, like HARRISON's pseudopotential, gives a value for these derivatives which is correct in sign but too small by a factor five. The Fermi level shifts in opposite direction to what is expected from the free electron case. One must therefore be very careful in drawing conclusions from simple models. There are several complications in a calculation of $(d \ln I_R/d \ln V)$ from the de Haas-van Alphen data. The volume dependence of the resistivity is even more sensitive than the resistivity itself to the location of the node of the form factor, for there is a cancellation effect from the contributions from either side of the node. The Fermi surface is not spherical, so we are not strictly limited to scattering processes with $(q/2\,k_F) \leqq 1$. Experimental errors in the de Haas-van Alphen data and the breakdown of the form factor description at reciprocal wavevectors add to the difficulties. Therefore we do not find a detailed numerical calculation very significant. Instead we use the de Haas-van Alphen data for $\mathscr{V}_{111}$ and $\mathscr{V}_{200}$ and their pressure derivatives to estimate $(d \ln I_R/d \ln V)$, as it comes from Eq. (1). With allowance for the uncertainties mentioned we find $0.5 \lesssim (d \ln I_R/d \ln V) \lesssim 3$.

Some quantities (the number of unit cells per unit volume, the free Fermi surface area and the length of q-vectors) were assumed to scale with the lattice spacing. One can have some doubt about this point, for the de Haas-van Alphen measurements mentioned gave a net change in the cross sectional area for some orbits that was twice that which would result from a pure scaling. However, we do not believe that the orbits considered are typical for the average behaviour of the Fermi surface. Remember that the number of electrons per unit cell is constant, so the Fermi surface encloses a constant volume in the reciprocal space.

For the remaining term, $(d \ln m_b/d \ln V)$, we have no reliable information. We will therefore assign to it a value which makes Eq. (2) hold. The result is summarized in the table. The errors given are somewhat arbitrary. They only serve the purpose of indicating which terms are best known, and the order of magnitude of the uncertainties. We will comment on the results in the next section.

Pressure Dependence of the Effective Mass

The value of $(d \ln m_{eff}/d \ln V)_T$ obtained from measurements of the low temperature thermal expansion of lead [4] is 1.0 ± 0.5. The value of λ for lead has been obtained by MCMILLAN and ROWELL [6] from tunneling experiments in superconductors. They find $\lambda = 1.5$. The term $(d \ln \Theta_\lambda/d \ln V)_T$ will be set equal to γ_G. The appendices should be seen, for a justification. Finally we make an estimate of $(d \ln I_\lambda/d \ln V)$ analogous to that used for the resistivity. In fact the only difference is an additional factor, q^2, in the integral for ϱ as compared to the integral for λ. Proceeding in the same way as for the resistivity we have estimated $1 \lesssim (d \ln I_\lambda/d \ln V) \lesssim 3$.

Several interesting conclusions can now be drawn. Although $(d \ln I/d \ln V)$ is very uncertain, there is no doubt that it is positive and can be quite large. The experimental results for $(d \ln \varrho/d \ln V)_T$ and $(d \ln m_{eff}/d \ln V)$ then both require that $(d \ln m_b/d \ln V)$ is negative and not very small in magnitude. The band mass is closely related to the form factor so it is natural that a strong volume dependence in one of them also leads to a strong volume dependence in the other. For a long time it has been thought that shifts in the phonon frequencies give the essential contribution to $(d \ln \varrho/d \ln V)$ in simple metals. Our analysis shows that there are other important contributions in lead but that they come in with opposite signs and almost cancel.

Nonlinear Temperature Dependence of the Resistivity

As the temperature is increased, the resistivity will increase due to the explicit temperature dependence as it appears in Eq. (1), but there will also be an additional effect coming from changes in the other quantities in the same relation. This additional variation will be very similar to the volume effect at constant temperature discussed above. At high temperatures the explicit temperature dependence gives a linear increase in the resistivity. For lead at room temperature there still remains a small correction to this linear behaviour from the exponential terms, but this correction can easily be estimated if the phonon spectrum is approximated by two Einstein peaks that are given the weights found in appendix 2. The explicit temperature dependence so evaluated is subtracted from the measured temperature coefficient for the resistivity. The rest can conveniently be expressed in the same form as Eq. (2) if we remember that the experiment is performed under constant pressure instead of constant temperature, i.e. if we consider that $(d \ln \varrho/d \ln V)_P$ and therefore $(d \ln \Theta_R/d \ln V)_P$ should contain both a volume effect and an additional purely anharmonic effect (cf. appendix 1). The rest of the terms in Eq. (2) comes only from the thermal expansion of the lattice. There are, however, some other differences as compared to the pressure effect at constant temperature. In our starting formula, Eq. (1), we have not included any Debye-Waller factor or multiphonon scattering processes. These two effects come in with opposite signs and it is still an open question whether they cancel exactly or not [13]. If they do not cancel, we can tentatively include them with an additional multiplicative factor $\exp(-\alpha T)$ in Eq. (1), leading to a term $-\alpha T (d \ln T/d \ln V)_P$ in Eq. (2). Simple estimates show [13] that any of the two effects considered separately gives a contribution to $(d \ln \varrho/d \ln V)_P$ which can be even larger than that coming from