and vanishes at the superconducting transition temperature. A semi-empirical formula for T_c has been obtained by McMillan (1968) using the strong coupling gap equations:

$$T_c = \frac{\theta_D}{1{\cdot}45} \exp\left\{\frac{-1{\cdot}04(1+\lambda)}{\lambda - \mu'(1+0{\cdot}62\lambda)}\right\} \tag{4}$$

where θ_D is the Debye temperature and λ the electron–phonon coupling strength defined in equation (2) of II; μ' is given by equation (2) above with $\omega_c = \omega_D$.

The calculation of the $\alpha^2(v)\,F(v)$ functions has been discussed in II. Phonon frequencies along the principal symmetry directions are calculated (see I) from a local AH model potential screened by the dielectric function of Shaw and Pynn (1969), and off-symmetry frequencies generated by a Kubic harmonic fit to these. The phonon polarization vectors are treated in an isotropic approximation and a one-orthogonalized plane wave matrix element used for the electron–phonon interaction. The pseudopotential μ^* has been calculated for both Thomas–Fermi and random phase approximations to the screened electron–electron Coulomb interaction.

An estimate of T_c can be obtained from McMillan's formula (4), but it does not provide a value of Δ_0 as well and so allow a study of the variation of the ratio of these quantities. The applicability of the formula is also somewhat restricted because the calculations on which it was based were performed for a fixed shape of $\alpha^2(v)F(v)$ and because it may not be reliable for very strong coupling metals such as Pb (McMillan 1968, Chen *et al.* 1969). We have therefore used this formula for predicting qualitative trends, but have also obtained Δ_0 and T_c as functions of pressure by solving the gap equations in detail.

Given values for $\alpha^2(v)\,F(v)$ and μ^*, the zero temperature gap equations (1) are readily solved by iteration and the gap edge Δ_0 determined from equation (3). For $T \sim T_c$, we have $\Delta(\omega') \sim 0$ so that the gap equations can be linearized, and again solved iteratively. As these equations are now only strictly valid for $T = T_c$, the transition temperature is found by seeking that temperature at which the iterations for $\Delta(\omega)$ are exactly convergent. Apart from possible systematic errors of up to $\pm$ 5% in T_c in Al, the numerical accuracy of our results for the superconducting properties is believed to be better than $\pm$ 1%.

3. Results and discussion

We first summarize the results of our calculation in II of the volume dependence of the electron–phonon coupling and discuss the calculation of the Coulomb pseudopotential. The corresponding changes in the superconducting properties of the metals are then studied and compared with experiment and with previous calculations.

3.1. *Electron–phonon and electron–electron interactions*

Although our method of calculation of the electron–phonon coupling $\alpha^2(v)F(v)$ and λ from given phonon frequencies and model potential is quite reliable, uncertainties in the theoretical potential, errors in the phonon dispersion curves calculated from them and so on imply an uncertainty of perhaps 20% in λ. For a fixed form of potential such systematic errors matter less, so that the calculated volume dependence of λ should be reliable as that of the phonons. Thus our results for Al, which are shown in figure 1, should be at least qualitatively accurate. The calculations for Pb underestimate the volume derivative of λ.

The Coulomb pseudopotential μ^* is slightly dependent upon the approximation used for the screened electron–electron interaction but the errors involved are considerably less than the uncertainties in our calculated values of λ. For each metal we neglect the slow decrease of μ^* with volume which, as can be seen from the results for Al in figure 1, is much less important than that of λ.

3.2. *Superconducting properties*

Points of reference for the solution of the superconducting gap equations are provided by using previously determined values of $\alpha^2(v)\,F(v)$. From McMillan and Rowell's (1965,

1969) experimental results for Pb, which were determined from effectively zero temperature tunnelling data, we find $\Delta_0 = 1{\cdot}34$ meV, $T_c = 7{\cdot}33$ K, and $2\Delta_0/k_B T_c = 4{\cdot}23$. The agreement of the last two quantities with experiment (Adler *et al.* 1967, Franck and Keeler 1967) indicates that the strong coupling gap equations give a consistent description of the superconducting properties of Pb at all temperatures, and provides a check on our numerical work. Similarly we find, from Carbotte and Dynes' (1968) calculated values of $\alpha^2(v)F(v)$ for Al, $\Delta_0 = 0{\cdot}188$ meV, $T_c = 1{\cdot}27$ K and $2\Delta_0/k_B T_c = 3{\cdot}44$. As we mentioned in § 2, there may be systematic numerical errors of up to 5% in T_c for Al. The calculated ratio of Δ_0 to T_c agrees reasonably with the BCS value of 3·52, as we would expect for this weak coupling superconductor, and also with experiment (Blackford and March 1968).

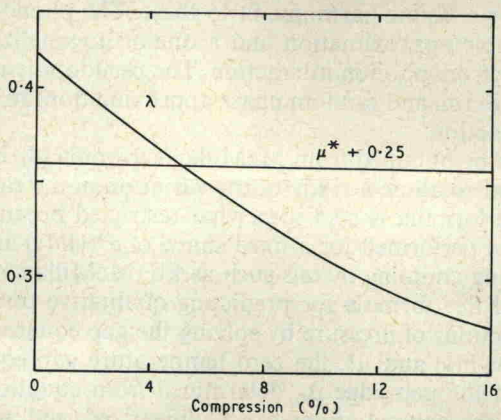

Figure 1. Volume dependence of calculated effective electron–phonon (λ) and Coulomb (μ^*) coupling strengths in Al.

We now turn to the results obtained with our calculated coupling functions. When the coupling strength is small, uncertainties in λ and μ^* imply large variations in the predicted T_c, as can be seen from equation (4). In Na, Shaw's potential provides the best description of the lattice dynamics (see I) and also the larger value of λ (II). Using our calculated μ^* of 0·13, we find $T_c < 10^{-4}$ K, but Allen and Cohen (1969) suggest that $\mu^* = 0{\cdot}16$ is a better estimate. Superconductivity is even less likely in *K* and, as λ decreases with volume, compression further lowers the probability of its occurrence in either.

As the transition temperature in Al is also quite sensitive to errors in the coupling constants, we first adjusted μ' from 0·105 to 0·12 so that McMillan's formula (4) yielded the measured transition temperature of 1·2 K at zero pressure. The volume dependence of T_c was then calculated from the values of λ in figure 1, and is shown in figure 2. The linear fit to the experimental points (Smith and Chu 1967) is also given and the agreement is seen to be reasonable. As with the phonon frequencies and elastic constants (see I), the theoretical pressure derivative is somewhat smaller than experiment. Upward deviations from linearity are evident in the theoretical curve beyond about 2% compression.

To verify these results, and also to study the behaviour of Δ_0, we have performed explicit calculations of T_c and Δ_0, using unadjusted values of μ^*, at compressions of 0, 2 and 4%. At zero pressure these yield $T_c = 1{\cdot}35$ K, $\Delta_0 = 0{\cdot}196$ meV and $2\Delta_0/k_B T_c = 3{\cdot}36$. In view of the errors and uncertainties in λ, this agreement with experiment is fortuitous. McMillan's formula yields $T_c = 2{\cdot}00$ K for the corresponding parameters, which partly reflects the limitations of equation (4) discussed above. The value of $2\Delta_0/k_B T_c$ agrees closely with that calculated from Carbotte and Dynes' $\alpha^2(v)\,F(v)$. For the finite compressions, this ratio changed by less than $\pm$ 0·01, while the values of Δ_0 and T_c continued to show nonlinear behaviour (see figure 2). The initial slope yields

$$\frac{\mathrm{d} \ln T_c}{\mathrm{d} \ln \Omega} = 14 \qquad \text{and} \qquad \frac{\mathrm{d} \ln T_c}{\mathrm{d}P} = -\,18 \times 10^{-6}\ \mathrm{bar}^{-1}$$