where we have used the P–Ω relation of Munson and Barker (1966), compared with the experimental values of 16 and -21 respectively in the same units (Smith and Chu 1967). In our approximate calculation by Hodder's (1969) technique in I, using a Lorentzian model for $\alpha^2(\nu)\,F(\nu)$, McMillan's formula (4) and the calculated pressure derivatives of the maximum phonon frequencies, we fortuitously obtained $\mathrm{d}\ln T_c/\mathrm{d}P = -20 \times 10^{-6}\ \mathrm{bar}^{-1}$ for Al. In subsequent calculations (Coulthard, Ph.D. thesis, University of London 1969,

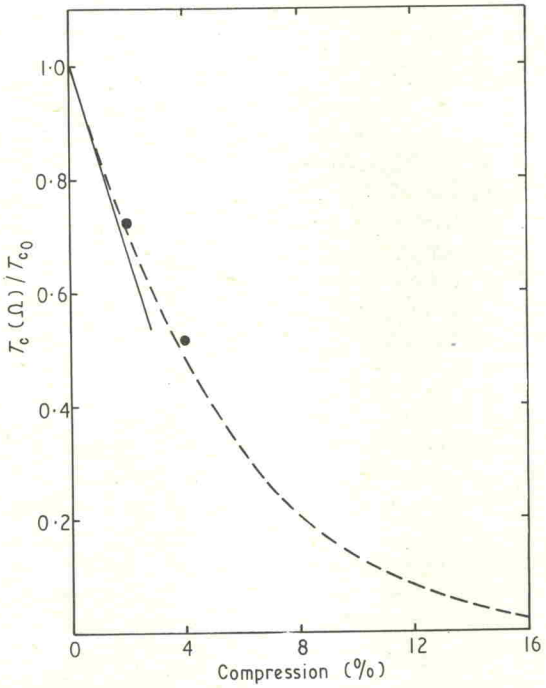

Figure 2. Volume dependence of transition temperature in Al. The full curve is the linear fit to the experimental points (Smith and Chu 1967). The broken curve is the calculation with McMillan's formula, for which $T_{c_0} = 1{\cdot}23$ K. The dots were obtained by direct solution of the gap equations with $\Delta_0 = 0{\cdot}196$ meV and $T_{c_0} = 1{\cdot}35$ K. For both $\lambda_0 = 0{\cdot}42$ while μ^* and $\mu' = 0{\cdot}12$.

unpublished) the integral for $\alpha^2(\nu)\,F(\nu)$ was simplified to one dimension by spherical averaging, but the volume dependence of λ was much the same as we found in II and we obtained $\mathrm{d}\ln T_c/\mathrm{d}P = -14{\cdot}5 \times 10^{-6}\ \mathrm{bar}^{-1}$ in Al. The errors in that and in the current results are due partly to those in the phonon pressure derivatives and partly to the fact that our calculated zero pressure transition temperatures were somewhat larger than the experimental value. Calculations with variable normalizations for λ and μ^* indicate that the logarithmic derivative of T_c will increase as T_c decreases. Therefore, once the zero pressure transition temperature is predicted correctly, we would expect the pressure derivative to agree quite well with experiment, as has been found by Trofimenkoff and Carbotte (1969).

The corresponding results for Pb are given in table 1. To reproduce the experimental zero pressure transition temperature of 7·2 K using McMillan's formula, we renormalized λ to 1·2, in good agreement with McMillan's (1968) empirical value, but considerably smaller than the directly measured value of 1·53 (Franck *et al.* 1969). The initial slope of the $T_c(\Omega)$ curve is then 20% larger than experiment, but this is partly due to the artificially small values of λ used. Small upward deviations from linearity are only evident for compressions of about 20%, for which the transition temperature has again been halved.

Direct solution of the gap equations using the calculated values of λ yields qualitative agreement with experiment, as can be seen in table 1. In particular, we note that the initial fractional change in Δ_0 is much larger than that in T_c, as found experimentally (Franck and Keeler 1968). That Pb, on compression, tends to behave more like a BCS superconductor is readily apparent from the sharp decrease in the ratio of Δ_0 to T_c. As with Al, these results differ little from those we obtained using a spherical averaging approximation in the coupling function, indicating that only the average effects of compression are of importance here.

Similar results for Pb and Hg were obtained by Trofimenkoff and Carbotte (1970) by rescaling the experimental $\alpha^2(\nu)F(\nu)$ using average experimental Gruneisen constants and rescreening of the AH potentials, as well as with first principles calculations of $\alpha^2(\nu)F(\nu)$ from experimental phonons and their pressure derivatives. This all confirms the average nature of the effect. For Al, they (1969) found an upward deviation from linearity in their $\Delta_0(\Omega)$ values for a compression of 5%. Calculations by Seiden (1969) and Kakitani (1969), using model forms for the electron–phonon interaction and McMillan's form of equation for T_c, have both predicted similar deviations from linear decrease with volume, but in all cases T_c was eventually pushed below presently measurable temperatures. We have obtained much the same results here in fully theoretical calculations of phonon frequencies, coupling functions and superconducting parameters.

4. Conclusions

As we discussed in II, the uncertainty in the electron–phonon coupling function arising from those in the screened model potential is considerable. By a serendipitous choice of potential and dielectric function from the many now available, one can obtain agreement with most experimental results, but reliable quantitative first principles calculations of superconducting transition temperatures are not possible at present. For instance, an error of 5% in λ in Al implies about a 20% change in T_c. However, the behaviour of simple metal superconductors as one parameter is varied may be accounted for. We have shown here that detailed calculations of $\alpha^2(\nu)\,F(\nu)$ can be used, in the strong coupling gap equations, to provide a qualitative first principles theoretical explanation of the observed changes under pressure of the superconducting parameters Δ_0 and T_c in Al and Pb. Going beyond the present range of experiments, our calculations predict that upward deviations will occur from the observed linear decrease of T_c with volume, but that superconductivity will probably still be eventually depressed below measurable temperatures. In the weak coupling superconductor Al the ratio of Δ_0 to T_c is found not to change with compression.

From our results in this series of papers we expect that, given a representation of the screened electron–ion potential that can account for the phonon dispersion curves of a particular simple metal, the strong coupling theory should then lead to a quantitative understanding of its superconducting properties. The success of Allen and Cohen (1969) in predicting transition temperatures for the hcp metals Zn and Cd using empirical pseudopotentials extracted from extensive Fermi surface data tends to confirm this expectation. The Coulomb vertex and renormalization corrections we mentioned in § 2 would have to be included in such calculations, as would higher order band structure corrections to $\alpha^2(\nu)\,F(\nu)$. However, the theoretical potentials available now are not sufficiently reliable for this to be meaningful.

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