

Table 6. Parameters for pressure dependence of transition temperatures

	Al		Pb	
	L	T	L	T
I_μ (mev ²)	120	27	14	6
ω_μ^2 (mev)	37	21.5	8.5	4.3
α_μ^2 (mev)	3.25	1.25	1.6	1.4
λ_μ	0.175	0.116	0.38	0.65
$d \ln I_\mu / dP$ (10^{-6} bar ⁻¹)	1.20	1.60	2.0	0.1
$d \ln \omega_\mu^2 / dP$ (10^{-6} bar ⁻¹)	2.9	2.75	5.0	4.0
λ	0.41 ± 0.01		1.7 ± 0.1	
$d \ln T_c / dP$ (10^{-6} bar ⁻¹)	-(20 ± 3)		-(1 ± 4)	

More detailed calculations of λ by Pytte (1967) and Trofimenkoff *et al.* (1968) both yielded values of 0.46 for Al, while Trofimenkoff *et al.* obtained 1.69 for Pb. From tunnelling measurements, McMillan and Rowell (1965) and Franck *et al.* (1969) deduced values of 1.34 and 1.53 respectively for Pb. Values of α_μ^2 for Pb have been obtained by Carbotte and Dynes (1968) from calculations— $\alpha_L^2 = 1.6$ and $\alpha_T^2 = 1.2$ —and by Rowell *et al.* (1969) from experiment— $\alpha_L^2 = 1.6$ and $\alpha_T^2 = 1.5$. For Al, Carbotte and Dynes' calculations yield $\alpha_L^2 = 2.8$ and $\alpha_T^2 = 1.1$. Considering the approximations involved, our results agree adequately with all previous work.

The peaks in the phonon density of states correspond to maxima in the phonon dispersion curves, so we can immediately calculate $d \ln \omega_\mu^2 / dP$ for the different branches. We have performed calculations for 1% compression of the metals and obtained pressure derivatives via the data in table 1. The average values, with likely errors for the local HA potential of $\pm 5\%$ for Al and 20% for Pb, are also included in table 6. The experimental values of Franck and Keeler (1967) for Pb are $d \ln \omega_\mu^2 / dP = 7.0 \pm 0.7$ and $d \ln \omega_T^2 / dP = 5.3 \pm 0.7$ in the same units. Our values agree poorly with these.

Taking $d \ln \omega_c / dP = d \ln \omega_\mu^2 / dP$, since $\omega_c \approx \omega_\mu^2$, equation (9) then yields, for Al,

$$\frac{d \ln T_c}{dP} = -(20 \pm 3) \times 10^{-6} \text{ bar}^{-1}$$

and for Pb,

$$\frac{d \ln T_c}{dP} = -(1 \pm 4) \times 10^{-6} \text{ bar}^{-1}$$

where the errors arise from estimates of the reliability, within the HA local approximation for the electron-ion model potential, of our results. In Al the $d \ln I_\mu / dP$ contribute 30% of the final value, compared with 10% in Pb, while errors in each are dominated by the uncertainties in the $d \ln \omega_\mu^2 / dP$.

From the experimental data summarized by Smith and Chu (1967) we find $d \ln T_c / dP = -22$ and $-5.3 \times 10^{-6} \text{ bar}^{-1}$ in Al and Pb respectively, with uncertainties of about 5%. Our result for Al therefore agrees quite well with experiment, and suggests that the pressure derivatives of the phonon frequencies near the zone boundary are also predicted satisfactorily by the local HA potential. For Pb, uncertainties in our calculated phonons are sufficiently great for our results not to be meaningful.

Hodder (1969) obtained $d \ln T_c / dP = -5.0 \times 10^{-6} \text{ bar}^{-1}$ for Pb, by using the Scalapino *et al.* (1965) fit for $F(\omega)$, McMillan and Rowell's (1965) estimates of α_μ^2 , Harrison's (1966) point ion pseudopotential, and Franck and Keeler's (1969) measured $d \ln \omega_\mu^2 / dP$; this is in very good agreement with experiment, but uncertainties and errors in these quantities amount to an uncertainty of about $\pm 30\%$ in the final result.

In another recent calculation of $d \ln T_c / dP$, Trofimenkoff and Carbotte (1969) calculated

$\alpha^2(\omega) F(\omega)$ in more detail. They used experimental phonon frequencies, scaled, for all q , by the experimental pressure derivatives of the sound velocities, and rescreened the HA potential at decreased volume. Their agreement with experiment for Al and Pb was good. We have checked this approximation in Al by substituting into (9) the calculated pressure derivatives of *small* q frequencies. Although the derivatives are 15% larger in the L branches and 3% smaller in the T branches, the differences cancel and $d \ln T_c/dP$ is altered by only 1%. This also shows that our calculation is not a sensitive test of the model potential. Seiden (1969) used a simplified model of the electron-phonon interaction to fit the zero pressure intercept and slope of the experimental curves for Al, Pb, Zn, Cd, In and Sn, and was able to extend his calculations beyond the range of current experimental results.

Our results for this calculation suggest that, with more careful first-principles calculations of $\alpha^2(\omega) F(\omega)$ and T_c , we should be able to explain quantitatively the observed behaviour of superconducting Al under pressure, without recourse to other experimental data. This work will be discussed later (Coulthard, to be submitted for publication). In Pb, the phonon dispersion curves cannot be calculated sufficiently reliably for such a programme to be completed at the present time.

5. Summary and conclusions

The HA and Shaw model potentials, as well as several forms for the exchange-correlation corrections to the dielectric function, have been studied by calculating the phonon dispersion curves and their pressure derivatives in the simple cubic metals Na, Al and Pb. This work is also effectively a test of the methods used for computing phonon frequencies from a model or pseudopotential. The main approximations there are the harmonic approximation in the dynamical matrix, and the calculation of the energy-wavenumber characteristic $F(q)$ just to second order in the potential.

We have, for these face-centred cubic and body-centred cubic metals, confirmed Shaw and Pynn's (1969) conclusion, from their calculations in hexagonal close-packed Mg, that inclusion of the exchange-correlation corrections is essential if the dispersion curves are to be predicted accurately. We have shown that the precise form of the function used to represent these corrections is also very important. The theoretically more probable forms yielded the better agreement with experiment, but the corrections need to be known more reliably at metallic densities before the model potentials can be assessed finally.

In Al, the dispersion curves and their pressure derivatives, calculated from the suitably screened HA local potential, are in good agreement with the experimental L branches, but the T frequencies are consistently relatively too large. The latter errors also occur, to a greater or lesser extent, in all previous calculations for Al and are due in part to uncertainties in the model potential for large q . Shaw's potential agrees closely with the equivalent HA potential near the L zone boundaries, but predicts C_{11} relatively closer to experiment. The entire T branches are also closer to experiment, although significant differences still exist. Inclusion of effective mass corrections further improves the dispersion curves.

The improvement due to Shaw's potential is even more marked in Na. Because of the lesser cancellation of ω_c^2 and ω_E^2 , this implies a considerable difference in the bare potentials. The HA potential again predicts the pressure derivatives of the elastic constants, with about the same errors as in the elastic constants themselves.

Our calculations therefore indicate that Shaw's modifications of the HA method have produced a more reliable bare potential. This potential, with an accurate dielectric function, effective mass corrections and this second-order method of calculating phonon frequencies, should account quantitatively for the observed structure and pressure dependence of the phonon dispersion curves in simple metals.

In Pb, spin-orbit effects and deviations of the Fermi surface and electron wave functions from their idealized behaviour are so important that the HA potential does not even yield qualitative agreement with experiment. The methods of calculating phonon frequencies will need to be revised extensively before reliable theoretical results can be obtained for such heavy simple metals.