Pressure dependence of phonon dispersion curves in simple metals⁺

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Abstract. The reliability of different forms for the bare electron-ion model pseudopotential and for the dielectric screening function has been studied by calculating, at variable volume, phonon dispersion curves in the simple metals sodium, aluminium and lead. We find that inclusion of exchange and correlation effect in the dielectric function is essential for agreement with experiment, and that the precise form of the corrections for these is also very important. Shaw's optimized non-local potential, when suitably screened, yields good agreement with experiment at zero pressure for sodium and aluminium, and better agreement than is obtained with the local version of the Heine–Abarenkov potential. Pressure derivatives of the elastic constants for these metals, as predicted from the Heine–Abarenkov potential, are reasonably accurate, while the pressure derivatives of the maximum phonon frequencies yield good qualitative agreement with the experimental pressure derivative of the superconducting transition temperature in aluminium. For lead, the agreement with experiment of the dispersion curves and pressure derivatives is generally poor.

1. Introduction

Before meaningful theoretical studies of complex properties of metals, such as the electronphonon interaction and superconducting transition temperatures, can be made, the reliability of the model potential or pseudopotential used to represent the electron-ion interaction must be known. In this paper we have used calculations of the phonon dispersion curves and their pressure derivatives to study these potentials for the simple metals sodium, aluminium and lead.

Estimates of the potential at the first few reciprocal lattice vectors can be obtained from fits to the Fermi surface as determined via de Haas-van Alphen experiments, but this is not sufficient to verify the accuracy of the potential at all values of momentum transfer. However, calculated phonon frequencies depend on the entire potential, so comparison of these with experiment provides a much more refined method of testing the various potentials suggested by different authors. Calculations at decreased volume permit a further check.

Many calculations of phonon dispersion curves in simple metals have been performed in recent years, using a variety of such electron-ion potentials. For instance, Vosko *et al.* (1965) used a single orthogonal plane wave approach for a non-local pseudopotential to calculate dispersion curves in Na, Al and Pb; Animalu *et al.* (1966) used a local Heine-Abarenkov (1964) model potential in calculations for the alkali metals and Al; and Shaw and Pynn (1969) used Shaw's (1968) optimized non-local model potential in a calculation for Mg. Calculations of the elastic constants have been performed by, among others, Shyu and Gaspari (1969), who used Ashcroft's (1966) local model potential for the alkali metals and Al.

Nearly all the calculations for the alkali metals agree well with the dispersion curves obtained from inelastic neutron scattering experiments. This is mainly because the conduction electron response to the vibrating ions, through which the pseudopotential enters the calculation, accounts for a relatively small proportion of the effective interaction between

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ions. Therefore, such calculations do not stringently test the various bare potentials and dielectric functions which have been obtained. In Al and Pb, however, conduction electron screening is much greater (on average, the actual phonon frequencies at the zone boundary are about 35% of the unscreened ionic lattice frequencies in Al, compared with 80% in Na), and the tests of modifications of the potentials are correspondingly more sensitive.

In most of this work we have used a local Heine-Abarenkov (1964, to be referred to as HA) model potential. Before dielectric screening this potential consists of a series of square wells of depth A_l for each angular momentum l, inside a radius R_M , and a Coulomb potential -Z/r outside this radius. The values of $A_l(E)$ at several values of energy E are obtained from spectroscopic data for the free atom and then extrapolated to the energy of the solid (which involves R_M). They set $A_l = A_2$ for l > 2. Shaw (1968) modified this by using a model potential only for those values of l for which there is an ionic core state, and by allowing R_M to vary with l and with energy. The potential was then variationally optimized according to the prescription of Cohen and Heine (1961). The full non-locality and energy dependence of the potential were included at all stages.

Using the local HA potential, we have calculated the dispersion curves for Na, Al and Pb, at variable volume, for a number of dielectric functions. These are discussed and compared with experimental zero pressure dispersion curves and pressure derivatives of the elastic constants in § 3. Where possible we have also performed calculations with Shaw's potential and with the 'semi-nonlocal'† version of the HA potential calculated by Animalu (1966). This gives an estimate of the differences in the bare model potentials. Shaw and Pynn (1969) have investigated the effects of the non-locality of the potential, and of exchange and correlation corrections to the dielectric function, on calculated phonon frequencies in hexagonal close-packed Mg. Our calculations for these cubic metals therefore supplement theirs, although we have studied the dielectric function more extensively. We have also estimated the effective mass corrections (Shaw 1969 b) to the dispersion curves in Al.

In §4 we have tested our calculated pressure derivatives of the maximum phonon frequencies by calculating the pressure derivatives of the superconducting transition temperatures of Al and Pb using Hodder's (1969) technique.

We conclude, in §5, that, when screened by a suitable dielectric function, the local HA potential is quite reliable in predicting these properties of simple metals, while the Shaw potential is even better where we have used it at zero pressure.

2. Theory and calculation details

In the harmonic approximation, the phonon frequencies $\omega^2(q, \mu)$ where q is the phonon wave vector and μ the polarization index, are the eigenvalues of the dynamical matrix $\mathbf{D}_{qB}(q)$. Along the principal directions of a cubic crystal they are given simply by

$$\omega^2(\boldsymbol{q},\mu) = \omega_{\rm c}^2(\boldsymbol{q},\mu) + \omega_{\rm R}^2(\boldsymbol{q},\mu) - \omega_{\rm E}^2(\boldsymbol{q},\mu).$$

The $\omega_c^2(q, \mu)$ arise from the direct Coulomb interaction between the (point) ions, and are treated by Ewald's method (Sham 1965). The contribution from the exchange overlap between cores, $\omega_R^2(q, \mu)$, is negligible in Na (Vosko 1964) and is expected to be small in Al and Pb also. It may be treated in the Born-Mayer approximation (Sham 1965) when necessary. The final term, $\omega_E^2(q, \mu)$, arises from the screening of the ions' vibration by the conduction electrons and is given by (Vosko *et al.* 1965)

$$\omega_{\rm E}^2(q,\mu) = \omega_{\rm P}^2 \sum_{H} \frac{(q+H)_{\mu}^2}{(q+H)^2} F(|q+H|) - \omega_{\rm P}^2 \sum_{H\neq 0} \frac{H_{\mu}^2}{H^2} F(|H|)$$
(1)

where the sums are over all reciprocal lattice vectors H of the crystal lattice, and $\omega_{\rm P}$ is the plasma frequency. The dependence upon the electron-ion potential is contained in this term.

† This includes some features of the non-local potential, but omits others; see Shaw (1969a).

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The energy-wavenumber characteristic F(q) is given, to second order in the HA model potential and in the 'semi-non-local' approximation, by (Animalu 1966).[†]

$$F(q) = \left\{ \frac{4\pi Z(1+\alpha_{\rm eff})}{\Omega q^2} \right\}^{-2} v(q) u_{\rm b}(q) \frac{\epsilon(q)-1}{1-f(q)}$$
(2)

where Ω is the atomic volume and Z the ionic charge. In the local approximation, the screened model potential $v(q) = u_b(q)/\epsilon(q)$, where the bare potential $u_b(q)$ is given by Animalu and Heine (1965) and the dielectric function is

$$\epsilon(q) = 1 + \{1 - f(q)\} (1 + \alpha_{\text{eff}}) \frac{\lambda}{2y^2} \left\{ 1 + \frac{1 - y^2}{2y} \ln \left| \frac{1 + y}{1 - y} \right| \right\}$$
(3)

where $y = q/2k_{\rm F}$, $\lambda = (\pi k_{\rm F})^{-1}$ and $(1 + \alpha_{\rm eff})$ is the orthogonalization hole correction factor introduced by Animalu and Heine (1965). In the theories of both Animalu *et al.* (1966) and Shaw (1969 a) a factor such as this appears in F(q) and in the plasma frequency because the ions are treated as having charge $Z(1 + \alpha_{\rm eff})$. It appears in $\epsilon(q)$ only when used with HA potentials, having been introduced by them to correct for an approximation in their treatment of the bare potential.

The function f(q) corrects for exchange and correlation effects among the conduction electrons. In the Hartree approximation f(q) = 0. From an approximate evaluation of higher order graphs, Hubbard (Falicov and Heine 1961) suggested that this correction could be approximated by

$$f_{\rm H}(q) = \frac{1}{2}y^2(y^2 + \beta)^{-1} \tag{4}$$

with

$$\beta_{\rm H} = \frac{1}{4}(1+4\lambda). \tag{5}$$

More recently, Geldart and Vosko (1965) chose β to satisfy a fundamental relation between the compressibility of an interacting electron gas and its dielectric function for $q \rightarrow 0$. Ashcroft (1968) and Shaw and Pynn (1969) have obtained a slightly different value of β in a similar calculation based on the Nozières-Pines (1958) interpolation formula for the energy of an interacting electron gas:

$$\beta_{\rm AS} = \frac{1}{2} (1 + 0.153\lambda)^{-1}. \tag{6}$$

Using the higher-order corrections to the exchange and correlation energies obtained by Ma and Brueckner (1968), Shaw found that an even better approximation for $q \rightarrow 0$ was given by

$$f_{\rm S}(q) = \frac{1}{2} \{1 - \exp(-2y^2)\} + \frac{4\gamma}{k_{\rm F}} y^2 \exp\left(-\frac{4\alpha k_{\rm F}}{\gamma} y^2\right)$$
(7)

with $\alpha = 0.0538$ and $\gamma = 0.0122$. Each of (4) and (7) have also been designed so that $\{1 - f(q)\} \rightarrow \frac{1}{2}$ as $q \rightarrow \infty$, implying that exchange corrections halve the effective interaction between electrons in this limit. However, Kleinman (1967, 1968) has argued that in fact $f(q) = O(q^2)$ for $q \rightarrow \infty$, in agreement with the correction factor he obtained from both self-consistent field and diagrammatic techniques:

$$f_{\mathbf{K}}(q) = \frac{1}{4} \left(\frac{y^2}{y^2 + \beta} + \frac{y^2}{\beta} \right).$$
(8)

Even more recent work by Langreth (1969) has confirmed this form for large q, but detailed calculations by Geldart and Taylor (1970 a, b) do not, so the subject is still open. In each case, the form of f(q) has simply been chosen to interpolate smoothly between the determined

† We use atomic units throughout.

limits for large and small q. The form of the correction factor for the intermediate range of q is still uncertain. We study the effects of these different forms for the dielectric function on the phonon dispersion curves in § 3.

For Shaw's non-local potential, the expression for the energy-wavenumber characteristic is much more complex (Shaw 1969 a), but reduces to (2) in the local approximation. Values for his F(q) for Na and Al, including dielectric screening via equations (3) and (7), (but excluding the factor $(1 + \alpha_{eff})$, as discussed above), have been tabulated by Shaw and Pynn (1969).

Band effective mass corrections are difficult to include (Shaw 1969b) and have been neglected throughout for simplicity. Although they are likely to have a significant effect on the calculated phonon frequencies, they should not affect our conclusions concerning the different dielectric functions. In §3.1, we have estimated their effects for Al, using an approximate calculation of Shaw (1969b).

In all calculations with the HA potential we have included the damping factor suggested by Animalu and Heine (1965) to decrease the oscillations for large q. This greatly improves the convergence of the sums over reciprocal lattice vectors in $\omega_{\rm E}^2$ and increases the Al phonon frequencies by less than 5%. For face-centred cubic lattices, summation over the 282 vectors with $|\mathbf{H}| \leq (40)^{1/2} 2\pi/a$, where a is the lattice constant, gave convergence of $\omega(\mathbf{q}, \mu)$ to 1 part in 10³, and for body-centred cubic lattices summation to $|\mathbf{H}| = (20)^{1/2} 2\pi/a$, 200 vectors, gave similar convergence.

3. Dispersion curves and elastic constants

For each of Na, Al and Pb we have calculated the phonon dispersion curves at compressions of zero and one per cent, using the forms of dielectric function based on equations (4) to (8) to screen the local HA model potential. In all calculations we have used the model potential parameters given by Animalu and Heine (1965) unless specifically stated otherwise, and have set the band effective mass equal to 1.00, as discussed above. Shaw's non-local optimized model potential, screened via (3) and (7), has also been used at zero pressure for Na and Al. As this potential has been developed from the HA method and is based on firmer theoretical foundations, we expect it to be the more reliable. The results discussed below bear this out.

As mentioned by Animalu and Heine (1965), the variation of the HA potential with volume depends mainly on the explicit volume factor in the bare potential and the variation of the dielectric function with $k_{\rm F}$. The remainder of the bare potential $u_{\rm b}(q)$ contributes only about 5% of the pressure derivatives of the phonon frequencies. However, the local potential is readily recalculated exactly at variable volume, so we have done that here. The volume dependence of the A_l parameters was found to have a negligible effect on the pressure derivatives of the phonon frequencies.

The elastic constants have been calculated directly from the initial slopes of the dispersion curves. In several calculations for compressions of up to 4% the pressure derivatives of the elastic constants varied by only small amounts with volume, so our values from 1% compression should be reliable. Both Stedman and Nilsson (1966) and Cowley *et al.* (1966) have noted that the initial slopes of their measured dispersion curves in Al and K respectively may differ by up to 5% from the sound velocities determined in ultrasonic experiments. These variations in the slope for very small frequencies affect only slightly the comparison of our results with experiment.

Relevant physical data and values of the different exchange–correlation parameters β for each metal are given in table 1. All are for a temperature of about 80 ° κ .

3.1. Aluminium

As Al is of the greatest interest for our calculations of superconducting transition temperatures, and its phonon frequencies depend sensitively upon the potential used to calculate them, it has been studied in more detail and will therefore be considered first. In table 2 we compare, with each other and with experiment, the frequencies of phonons at the zone boundaries calculated using the different bare potentials and dielectric functions. We denote the longitudinal branches by L and the transverse branches by T_1 and T_2 . The elastic constants and their pressure derivatives are treated similarly in table 3.

Table 1. Physical data and exchange-correlation parameters β at 80° K

	Unit	Na	Al	Pb
Volume of unit cell	a_0^3	254.5	110.7	203.4
Fermi wave number	a_0^{-1}	0.4882	0.9293	0.8351
Density	g cm ⁻³	1.01	2.73	11.50
Pressure to produce 1% compression	$10^8 \mathrm{Nm^{-2}}$	0.70 ^a	7.50 ^b	4.04 ^b
$\beta_{\rm H}$ (equation (5))		0.902	0.593	0.631
β_{AS} (equation (6))		0.454	0.475	0.473

 a_0 is the Bohr radius (= 0.5292 Å). a, Beecroft and Swenson (1961); b, Munson and Barker (1966).

	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1		100 L	100T	111L	111T
Experiment ^a			6.08	3.65	6.06	2.63
potential	f(q) (author and num equatio	β nber of relevant n in text)				
1. HA local	none		7.78	4.68	8.04	3.27
2. HA local	Hubbard (4)	Hubbard (5)	6.76	4.40	6.73	3.25
3. HA local	Hubbard (4)	Ashcroft and Shaw (6)	6.55	4.36	6.44	3.25
4. HA local	Shaw (7)	Ashcroft and Shaw (6)	6.37	4.29	6.26	3.25
5. HA local	Kleinman (8)	Ashcroft and Shaw (6)	6.13	4.11	6.01	3.20
6. HA local A, adjusted	Shaw (7)	Ashcroft and Shaw (6)	6.09	3.67	6.13	2.89
7. Shaw non-local	Shaw (7)	Ashcroft and Shaw (6)	6.32	4.00	6.40	2.82

Table 2. Al phonon frequencies at the zone boundaries in units of 10^{13} rad s⁻¹

a, Stedman and Nilsson (1966), at 80°K.

	<i>C</i> ₁₁	$\mathrm{d}C_{11}/\mathrm{d}P$	C44	dC_{44}/dP	C'	dC'/dP
Experiment ^{a, b}	1.14	6.9	0.31	2.3	0.26	1.7
1. 1. 1. 1. 1. 1.	1. 1.92	8.5	0.57	2.8	0.32	1.6
	2. 1.20	7.3	0.50	3.0	0.36	1.7
	3. 1.02	7.2	0.49	3.0	0.37	1.7
Calculations ^c	4. 1.02	7.3	0.47	3.0	0.38	1.8
	5. 0.98	7.3	0.42	3.0	0.39	1.8
	6. 0.86	6.5	0.39	2.5	0.27	1.3
	7. 1.06	CU <u>AR</u> SHIP	0.43	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0.25	S AL BULL

Table 3. Al elastic constants (in units of 10¹¹ Nm⁻²) and pressure derivatives

a, Kamm and Alers (1964), Vallin *et al.* (1964), at 80° κ ; b, Ho and Ruoff (1969), at 77° κ ; c, see table 2 for potential, f(q) and β used for each set.

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We first use the local HA potential to study the effects of different dielectric functions. When the exchange-correlation correction f(q) to the dielectric function is neglected (line 1 in tables 2 and 3) the phonon frequencies are 25% larger than experiment, and the elastic constants at least as much in error. Inclusion of the Hubbard correction function (4) and (5) immediately halves these errors (line 2) and shows the essential nature of such corrections.

Altering the value of β to β_{AS} (equation (6)), which is a theoretically more probable value, decreases the errors again (line 3). Further, Shaw's form (7) for f(q), with effectively the same value of β and same large q limit, gives significantly different results (line 4), while Kleinman's form (8), which has a different large q limit, decreases the frequencies still more (line 5). Theoretically, the most probable form for f(q) that can be suggested now would differ from Shaw's form for large q and would produce results lying between those of lines 4 and 5.

We see, then, that the variations due to the different correction functions are almost as large as those due to neglecting it altogether. Thus it is important that the precise form of these corrections be known more accurately, particularly for intermediate q, before the bare model potential can be assessed conclusively.

Although Kleinman's f(q) here produces the best agreement with the experimental phonon frequencies at the zone boundaries, the inclusion of effective mass corrections (see below) will alter the situation. The relative behaviour of the different forms for f(q)is unlikely to be changed, however. Even when the L branches are close to experiment (line 4), the T branches are consistently about 20% too high. The elastic constants are sensitive to β rather than to the form of f(q). C_{11} and its pressure derivative agree well with experiment, but the transverse branches are again far too large. Relative to the phonon frequency at the [100L] zone boundary the HA potential consistently predicts values of C_{11} which are too small. Overall, then, the dispersion curves and their pressure derivatives, calculated from the local HA potential, agree reasonably with experiment, but quite



Figure 1. Phonon dispersion curves in Al. The full curves are those calculated with Shaw's potential screened by a dielectric function including his correction function (7). The broken curves are those calculated with the local HA potential, screened by the same dielectric function. The experimental points are taken from Stedman and Nilsson (1966). The wave vector q is plotted in units of $2\pi/a$, $(2)^{1/2}2\pi/a$ and $(3)^{1/2}2\pi/a$ in the [100], [110] and [111] directions respectively.

large discrepancies exist in the T branches. The dispersion curves calculated using Shaw's correction function (7) in the screening of this potential are shown in figure 1, together with the experimental values, at 80° K, of Stedman and Nilsson (1966).

The results can be quite sensitive to variations in the A_l parameters, a change of 1% in A_l altering the frequencies by 5%. This suggests that uncertainties in extrapolating the $A_l(E)$ to the energy of the solid may ultimately limit the reliability with which one could calculate dispersion curves from a model potential based on the HA method. By adjusting the A_l parameters slightly, (to 1.37, 1.635, 1.75 for l = 0, 1, 2 respectively, compared with the HA values of 1.38, 1.64 and 1.92) the phonon frequencies at the zone boundary can be brought much closer to experiment (line 6), although the elastic constants are not thereby improved greatly. Such a fitting adds little to our understanding of the fundamentals of the situation, however.

Calculations with the semi-non-local HA potential of Animalu (1966) agree closely with those for the local potential with the same dielectric function (line 1), so non-locality must be included fully for its effects to be evident.

The effects of changing the bare potential can be seen from the dispersion curves calculated with Shaw's potential, with exchange-correlation corrections (7) (Shaw and Pynn 1969). They are included in figure 1, with the results for the HA potential screened by the same dielectric function, and are also given in line 7 of the tables 2 and 3. Correcting the atomic volume Shaw used, from 300 to 80 °K, would marginally increase the frequencies. Shaw's L branches are almost identical with the HA ones (line 4) at the zone boundaries, but the predicted value of C_{11} is relatively closer to experiment. His T branches are also significantly closer to experiment, although errors of about 10% still exist. Similar errors, relative to the L branches, were also obtained by Vosko *et al.* (1965) and all appear to be due in part to uncertainties in the short range, that is large q, behaviour of the potential. This is suggested by the facts that the Kleinman f(q) and the HA damping factor both affect the T frequencies more than the L, even though the cancellation of ω_c^2 by ω_E^2 is greater for the L branches.

The effects of the different forms for f(q) on Shaw's potential can be studied by using equation (2.4) of Shaw and Pynn (1969). Neglect of the corrections increases the frequencies by 15-20%, so they are again essential, while the results are only slightly less sensitive to variations in f(q) than for the HA potential. Modification of the correction function for large q via equation (8) again improves agreement with experiment.

Shaw has performed calculations of his potential at only one value of the volume for each metal, so we have not been able to calculate pressure derivatives of the elastic constants. We hope to do that later.

We have therefore confirmed Shaw and Pynn's conclusion that inclusion of exchangecorrelation corrections in the screening is essential for all metals, and have shown that the precise form of these corrections is also very important. The relative trends using the different bare potentials are the same as those obtained by Shaw and Pynn for Mg, and indicate that the optimized non-local potential is a definite improvement over the local HA potential.

Two other refinements we should consider are the exchange overlap terms ω_R^2 and the effective mass corrections. In Al, the nearest neighbour distance is about 6 ionic radii, compared with 3 in Na. Therefore we expect the ω_R^2 to remain negligible, even though the cancellation of ω_c^2 and ω_E^2 is greater in Al. In fact, using plausible values for the overlap potential parameters, we find that these terms increase the phonon frequencies and pressure derivatives by less than 2%. The inclusion of effective mass corrections has been discussed by Shaw (1969 b). He gave approximate values for the resulting change in the energy-wavenumber characteristic F(q) screened by a Hartree dielectric function. We find that these corrections decrease the L and T frequencies at the [100] zone boundary from 7.8 to 7.2 and 4.6 to 4.3 respectively, with similar changes in all branches. Such corrections should therefore improve still further the dispersion curves calculated with the properly screened Shaw potential (line 7).

We cannot immediately compare our results with those of Animalu *et al.* (1966) since they set $A_2 = Z/R_M = 1.50$ in their local HA potential. This change in A_2 decreases the magnitude of oscillations in the potential for large q and, as they remarked, does not affect greatly the values of the potential at the reciprocal lattice vectors. It does, however, change the phonon frequencies markedly, particularly in the 100T branch. As this change is almost ten times larger than that caused by the HA damping factor, we feel that our approach gives a better estimate of the reliability of the original HA method.

The only other calculation with which we can compare our elastic constants is that of Shyu and Gaspari (1969) who used a local Ashcroft potential, screened via Hubbard's f(q), to obtain $C_{11} = 0.78$ for Al. Our most reasonable value, as predicted by the local HA potential, was 1.02, while Shaw's potential gave 1.06. Even allowing for its overestimation of the rest of the [100L] branch, Shaw's result is better than the others, so we can hope to improve the pressure derivatives also by using his potential.

3.2. Sodium

The corresponding Shaw and HA dispersion curves for Na, together with the experimental values, at $80^{\circ}\kappa$, of Woods *et al.* (1962), are shown in figure 2. Again the overall agreement of Shaw with experiment is good, and better than HA.



Figure 2. Phonon dispersion curves in Na. The full and broken curves represent calculations with the potentials corresponding to those in figure 1. The experimental points are taken from Woods *et al.* (1962). Units for the wave vector are also as in figure 1.

In Na, ω_c^2 and ω_E^2 do not cancel to the same degree as in Al, so the effects of any variations in the potential are not as pronounced. With both the Shaw and HA bare potentials, neglect of the exchange-correlation corrections in the dielectric function increases the L phonon frequency at the [110] zone boundary by 10% and the L elastic constants by 50%, but leaves the rest of the dispersion curves virtually unaltered (see tables 4 and 5). The different values of β yield results lying between these, with very little dependence on the actual form of f(q). Therefore it is again necessary that these effects be included, while our results suggest that β_{AS} may again be preferable to β_{H} .

As in Al, Animalu's semi-non-local potential (1966) agrees closely with HA local. Comparing lines 1 and 2 in the tables 4 and 5, we see that Shaw's potential represents a distinct improvement, relative to experiment, over the local Ha potential. The elastic constants for

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			100	110L	110T ₁	110T ₂
Experiment ^a			2.25	2.40	0.58	1.61
Calculations: potential	f(q) (author an relevant eq	β nd number of mution in text)				
1. Shaw	Shaw (7)	Ashcroft and Shaw (6)	2.37	2.59	0.52	1.63
2. HA local	Shaw (7)	Ashcroft and Shaw (6)	2.73	3.11	0.68	1.81
3. HA local	none	in indexation	2.73	3.32	0.67	1.80
4. HA + $\omega_{\rm R}^2$	Shaw (7)	Ashcroft and Shaw (6)	2.77	3.12	0.68	1.83

Table 4. Na phonon frequencies at the boundaries in units of 10¹³ rad s⁻¹

a, Woods et al. (1962), at 90°K.

Table 5. Na elastic constants (in units of 10⁹ Nm⁻²) and pressure derivatives

	<i>C</i> ₁₁	$\mathrm{d}C_{11}/\mathrm{d}P$	C44	dC_{44}/dP	C	$\mathrm{d}C'/\mathrm{d}P$
Experiment ^a	8.6	4.2	5.9	1.2	0.73	0.26
	1. 8.1	—	5.9	1979 <u>—</u> 1979	0.58	1-1
Calculations ^b	2. 11.4	4.8	7.3	1.6	1.00	0.3
	3. 17.7	6.2	7.2	1.6	0.97	0.3
	4. 10.6	4.9	7.5	1.8	1.00	0.3

a, Martinson (1969), at 80° κ ; b, see table 4 for potential, f(q) and β used for each set.

Shaw agree to within 5% with experiment, except for C' which is 20% too small. The HA potential, with Shaw's f(q) in the screening, produces reasonably accurate elastic constants and pressure derivatives, considering the errors at the zone boundaries.

An estimate of the importance of the ω_R^2 can be obtained by using the Bleick-Mayer potential (Vosko 1964) for the exchange overlap interaction between Ne atoms. The results are given in line 4 of the tables 4 and 5. As Vosko argued, the interaction in metalic Na would be smaller by at least a factor $\frac{1}{16}$. Even without that reduction, the frequencies are altered by less than 2% and the pressure derivatives of the elastic constants by less than 5%, so we can certainly neglect the effect altogether. Effective mass corrections will probably have as small an effect in Na as the corrections to the dielectric function.

Compared with previous calculations, Shaw's phonons are rather closer to experiment than those of Vosko *et al.* (1965), but not quite as good as Ashcroft (1968) obtained with his local model potential. Ho (1968) fitted parameters in his local potential to reproduce the experimental elastic constants, but his errors at the zone boundaries are much the same as for the Shaw potential. Shyu and Gaspari (1969) obtained $C_{11} = 9.6$ for Na, much the same as we have calculated with the HA potential, and also further from experiment than Shaw. Suzuki *et al.* (1968) fitted Ashcroft's potential to the experimental elastic constants and then found that their calculated pressure derivatives were less than 4%from experiment. Wallace (1968) fitted his potential to the measured crystal binding energy and its first two volume derivatives. His dispersion curves are then very good except for differences in the [110] branches of the same magnitude as Shaw's and Ho's.

Shaw's first-principles potential is thus as good as any of those which have been explicitly fitted to some experimental phonon data, and better than the local HA potential. We can therefore expect that it would also predict the pressure derivatives accurately. The calculations of Bortolani and Pizzichini (1969) for Li show that the inclusion of non-locality in the HA potential improves it significantly. This could also occur for Na. We should note

that their criticisms of Shaw's potential for Li do not apply to Na because Shaw modelled both the l = 0 and l = 1 components here.

Finally, we remark that the dispersion curves for K, calculated with Shaw's potential, agree exceptionally well with the experimental values, at 9° K, of Cowley *et al.* (1966) (see figure 3). The relative errors of the HA potential are the same as for Na and the exchange–correlation corrections have similar significant effects, so we need not discuss these curves further.



Figure 3. Phonon dispersion curves in K. The full and broken curves are again as in figure 1, and the experimental points are from Cowley *et al.* (1966). Units for the wave vector are as in figure 1.

3.3. Lead

The dispersion curves for Pb, calculated from the local HA potential, are, at best, in only qualitative agreement with experiment. Shaw has not calculated his potential for any element as heavy as Pb.

When the A_i parameters of Animalu and Heine (1965) are used, the lower part of the $[110T_1]$ branch is imaginary, the peaks in the [100] branches are far too small and the phonon frequencies at the zone boundaries are too high, regardless of the dielectric function used. Because of the even greater cancellation of ω_c^2 and ω_E^2 than in Al, the effects of the different forms for f(q) are greater, but the trends are much the same. The dispersion curves calculated with Animalu's semi-non-local potential have more pronounced peaks in the [100] branches but are otherwise unaltered. The nearest neighbour distance in Pb is greater than four core radii, so we again expect the ω_R^2 contributions to be relatively unimportant. Effective mass corrections should be significant, but are unlikely to account for the differences from experiment.

Satisfactory agreement with experiment cannot be obtained even when the A_l parameters are varied arbitrarily, and the pressure derivatives of the elastic constants agree poorly with experiment (Miller and Schuele 1969). This form of potential therefore cannot be used to calculate reliably the phonon dispersion curves in Pb. Vosko *et al.* (1965) and

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Harrison (1966) also could only obtain qualitative agreement with experiment by adjusting parameters in their potentials. As they pointed out, spin-orbit effects and effects due to the real Fermi surface and electron wave functions would be important in Pb and would have to be included in any proper theoretical treatment of its phonon dispersion curves.

4. Pressure dependence of maximum phonon frequencies and superconducting transition temperatures

We conclude the study of the model potentials by testing the predicted pressure derivatives of the maximum phonon frequencies for the different branches. They have been used to calculate the pressure derivative of the superconducting transition temperatures, $T_{\rm c}$ of Al and Pb, following a method Hodder (1969) has used for Pb. We shall simply outline Hodder's technique here and indicate how we have used it, leaving all detailed discussion of the pressure dependence of $T_{\rm c}$, both experimental and theoretical, to a later paper in which results of our detailed study of the electron-phonon interaction and superconductivity will be given (Coulthard, to be submitted for publication).

Hodder's (1969) technique is based on McMillan's (1968) formula for T_c and an approximation of the phonon density of states $F(\omega)$ by a superposition of Lorentzians. Assuming that only the peaks, ω_1^{μ} , of the Lorentzians move under pressure, he obtained:

$$\frac{d\ln T_{\rm c}}{dP} = \frac{d\ln\omega_{\rm c}}{dP} + \frac{1.23}{(\lambda - 0.11)^2} \sum_{\mu=1}^{3} \lambda_{\mu} \left(\frac{d\ln I_{\mu}}{dP} - 2\frac{d\ln\omega_{1}^{\mu}}{dP} \right)$$
(9)

where

$$\lambda = \sum_{\mu=1}^{3} \lambda_{\mu} = \sum_{\mu=1}^{3} 2 \int_{0}^{\infty} \alpha_{\mu}^{2}(\omega) F_{\mu}(\omega) \frac{\mathrm{d}\omega}{\omega}$$

 $\alpha^2(\omega) F(\omega)$ is the electron-phonon coupling function (Scalapino *et al.* 1966), ω_c is the maximum phonon frequency, and I_{μ} depends upon the electron-ion potential:

$$I_{\mu} = \frac{m^*\Omega}{8\pi^2 k_{\rm F}} \int_0^{2k_{\rm F}} \langle (\boldsymbol{\epsilon}_{\boldsymbol{q}\mu} \cdot \boldsymbol{q})^2 \rangle_{\rm av} \, v^2(\boldsymbol{q}) \, \boldsymbol{q} \, {\rm d}\boldsymbol{q}.$$

The electron–electron Coulomb pseudopotential has been set equal to 0.10, and the frequency dependence of $\alpha_{\mu}^{2}(\omega)$ for each mode μ will be neglected.

In deriving equation (9), Hodder (1969) assumed that $(\omega_2^{\mu}/\omega_1^{\mu})^2 \ll 1$, where ω_2^{μ} is the half-width of the Lorentzian. Making the same approximation in his equation (5) for λ_{μ} , we obtain

$$\lambda_{\mu} \simeq \frac{2\alpha_{\mu}^2}{\omega_1^{\mu}}$$

while $\alpha_{\mu}^2 = I_{\mu}/\omega_1^{\mu}$ from his equation (8). These equations are equivalent to McMillan's (1968) equation (39), and show that the coupling depends on the model potential mainly through the phonon frequencies. The value of d ln T_c/dP from (9) is dominated by ω_1^{μ} and d ln ω_1^{μ}/dP , because we find d ln I_{μ}/dP to be relatively small, so we have an immediate test of our calculated phonon pressure derivatives.

The parameters for the Lorentzian fits to $F(\omega)$ were chosen to reproduce as well as possible the experimental $F(\omega)$ of Stedman *et al.* (1967). For Al, we used $\omega_1^L = 37$, $\omega_2^L = 2$, $\omega_1^T = 21.5$ and $\omega_2^T = 5.3$ meV, and for Pb, 8.5, 0.5, 4.3 and 1.5 respectively; $\omega_3^{\mu} = 2\omega_2^{\mu}$ throughout. The I_{μ} integrals have been calculated using the same model potentials as for the phonons; exchange-correlation corrections in the dielectric function are again important, amounting to 20% of I_{μ} , but affecting the logarithmic derivatives by only about 5%. Our values for the I_{μ} , d ln I_{μ}/dP , α_{μ}^2 and λ are given in table 6. Likely errors, within the local HA potential approximation, are $\pm 3\%$ for Al and $\pm 10\%$ for Pb. Harrison's (1966) point ion potential yielded values of I_{μ} which were 10–20% larger, while Shaw's non-local potential predicts values 5–10% smaller than those in the table.

Table 6. Parameters for pressure dependence of transition temperatures

	1	41	Pb		
	L	Т	L	Т	
$I_{\mu} (\mathrm{mev}^2)$	120	27	14	6	
ω_1^{μ} (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	
$d \ln I_{\mu}/dP (10^{-6} \text{ bar}^{-1})$	1.20	1.60	2.0	0.1	
$d \ln \omega_1^{\mu} / dP (10^{-6} \text{ bar}^{-1})$	2.9	2.75	5.0	4.0	
λ	0.4	1 ± 0.01	1	$\cdot 7 \pm 0.1$	
$d \ln T_{\rm c}/dP (10^{-6} {\rm bar}^{-1})$	-($20 \pm 3)$		$-(1 \pm 4)$	

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 $\ln \omega_1^{\mu}/dP$ 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 $\ln \omega_1^{L}/dP = 7.0 \pm 0.7$ and d $\ln \omega_1^{T}/dP = 5.3 \pm 0.7$ in the same units. Our values agree poorly with these.

Taking d ln $\omega_c/dP = d \ln \omega_1^L/dP$, since $\omega_c \simeq \omega_1^L$, equation (9) then yields, for Al,

$$\frac{d \ln T_{\rm c}}{dP} = -(20 \pm 3) \times 10^{-6} \, \rm{bar}^{-1}$$

and for Pb,

$$\frac{d \ln T_{\rm c}}{dP} = -(1 \pm 4) \times 10^{-6} \, \rm{bar}^{-1}$$

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_{μ}/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 ω_{\perp}^{μ}/dP .

From the experimental data summarized by Smith and Chu (1967) we find d ln $T_c/dP = -22$ and -5.3×10^{-6} 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 ω_1^{μ}/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. The approximate calculation of the pressure derivative of the superconducting transition temperature in Al suggests that the model potential also predicts the pressure derivatives of the higher phonon frequencies adequately, and that the strong coupling theory of superconductivity can be used to explain the behaviour of superconductors under pressure. This can only be confirmed accurately by detailed calculations of the electron-phonon coupling function and the superconducting transition temperatures. Such a study is currently being completed.

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