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A modified Ashcroft pseudopotential: application to aluminium

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Abstract. Unified study of the different properties of metals clearly reveals the inadequacy of the empty-core Ashcroft pseudopotential even in the case of simple metals. In the present paper we propose a modification of the one-parameter Ashcroft pseudopotential by assuming the parameter r_c to be wave vector-dependent. This introduces a simple modification of the electron-ion pseudopotential in the reciprocal space. The corresponding potential in the configuration space shows that the abrupt change in the Coulomb potential at $r = r_c$ is replaced by a continuous change spread over a small region near the core boundary. The present model has been used to make a unified study of Al and is found to be a significant improvement over the simple Ashcroft model. The agreement between the calculated and experimental values is found to be quite satisfactory.

Keywords. Modified Ashcroft pseudopotential; unified study; Taylor's dielectric function; Vashishta-Singwi dielectric function.

1. Introduction

In a recent investigation, Sen *et al* (1980) have pointed out that the empty-core Ashcroft (1966) pseudopotential is not suitable for unified studies even in the case of simple metals. Though they obtained fair agreement for the static properties of the alkali metals, the discrepancy in the case of phonon dispersion was about 40% in some cases. Price *et al* (1970) attempted to calculate the different properties of alkali metals on the basis of Ashcroft's model. But in order to obtain reasonable agreement with the experimental values they had to use two different values for the same parameter in the first and the second order energy expressions respectively. All these studies clearly indicate the inadequacy of the empty-core Ashcroft pseudopotential for a comprehensive unified study and it seems evident that in order to obtain reasonable agreement with the experimental values for both the static and dynamic properties of a crystal, one has to use two different values of the same parameter. But from a theoretical standpoint this is inconsistent and does not make sense as a pseudopotential. In the present paper we have modified the Ashcroft pseudopotential by assuming the parameter of the potential to be wavevector dependent and the dependence is assumed in such a way that in the short and long wavelength limit we get two distinct constant values of the parameter. This introduces a simple modification for the Fourier transform of the potential and makes the model consistent. The potential in the direct space has also been evaluated. The modified potential has been used to make a unified study of Aluminium. For the present purpose we have felt it sufficient to limit our calculations to one typical simple metal Al, because of the reasons mentioned below.

Aluminium is a close-packed, simple polyvalent metal. The area of the Fermi surface of this metal, and its general topology, do not really deviate very much from the free electron sphere. The small pockets of holes and the reefs and islands of zone boundary projecting through the surface, do not make any significant contribution to the thermodynamic properties as the total area of the free surface is very large. From an analysis of the results of measurements of the Fermi surface in Al, it is possible to conclude that non-locality plays a very small role in the effective electron-ion interaction (Ashcroft 1963; Kimball *et al* 1967 and Lee 1966). Again the role of higher order terms giving rise to non-pairwise forces is not so important in reproducing the phonon frequencies of this metal (Williams 1973; Bertoni *et al* 1974, 1975). In the long wave method, however, the contribution of the third and fourth order terms to the elastic constants is significant (Bertoni *et al* 1974; Brovman and Kagan 1974). But a homogeneous deformation theory confined up to the second order perturbation terms effectively includes terms up to the fourth order of long wave approach (Brovman and Kagan 1974; Wallace 1969). Thus Al appears to be one of the few polyvalent elements for which local model potentials with second order perturbation theory can be used with confidence provided the elastic constants are calculated by the method of homogeneous deformation. Moreover, an initial attempt to make a unified study of the lattice mechanics of simple metals using Ashcroft pseudopotential shows that the results are more disastrous in the case of Al. When the parameter of the Ashcroft pseudopotential is determined from the equilibrium condition, the model is found to reproduce the static properties of the alkali metals fairly well, whereas a discrepancy of about 40% is observed in the case of zone-boundary phonons. But a similar calculation repeated in the case of Al gives elastic constants which are about four to five times the experimental values. All these facts justify our choice of Al as the representative metal. As the suitability of a potential can be judged only through a comprehensive unified study, we have used the modified Ashcroft pseudopotential to study the different properties like the cohesive energy, equilibrium lattice parameter, second order elastic constants and their pressure derivatives, equation of state and the phonon dispersion along the symmetry directions for Al. Previously, Das *et al* (1980) have made a unified study of alkali metals using this modified Ashcroft pseudopotential and obtained encouraging results.

2. The modified Ashcroft pseudopotential

The Ashcroft pseudopotential in r-space is given by

$$\begin{aligned} V(r) &= 0, \qquad r < r_c \\ &= -\frac{Ze^2}{r}, \quad r > r_c, \end{aligned} \tag{1}$$

r_c being the parameter of the potential. The Fourier transform of this potential is correspondingly given by

$$V(q) = -\frac{4\pi Ze^2}{\Omega q^2} \cos q r_c, \tag{2}$$

where Ω is the volume per ion and Z is the valency.

We propose a simple modification of this potential in q-space by assuming r_c to be q-dependent and write it in the form

$$r_c(q) = r_{c1} + (r_{c2} - r_{c1})\ (1 - \exp(-q^2/q_0^2)), \tag{3}$$

In (3) r_{c1} and r_{c2} are the two parameters of the modified potential and q_0 is an arbitrary parameter, the value for which in the present calculation is chosen to be $10^{-2}\ \pi/a$, $2a$ being the lattice constant. It may be pointed out that the calculated properties are insensitive to the value of q_0 chosen provided it is sufficiently low. It may be remarked here that r_{c1} and r_{c2} are the two values of $r_c(q)$ in the long and short wavelength limit respectively, *i.e.*, $r_c(0) = r_{c1}$ and $r_c(q) = r_{c2}$ for $q \gg q_0$.

The potential in r-space corresponding to this modified pseudopotential is given by

$$V(r) = -\frac{2\,Ze^2}{\pi\, r} \int_0^\infty \cos\,(q\, r_c(q)) \frac{\sin qr}{q}\, dq. \tag{4}$$

We have numerically computed the potential for Al which is shown in figure 1. The potential in r-space is found to be continuous and except in a small region near the boundary of the core it is found to be zero everywhere inside the core.

3. Energy of a metallic solid

For simple metals having Z valence electrons per ion, the second order pseudopotential theory expresses the static energy per ion as

$$U = Z\, E_g + Z\, E_N + E_{es} + E_B. \tag{5}$$

Here the first two terms are purely volume dependent energies. E_g includes the kinetic, exchange and correlation energies. In the present calculation we have con-

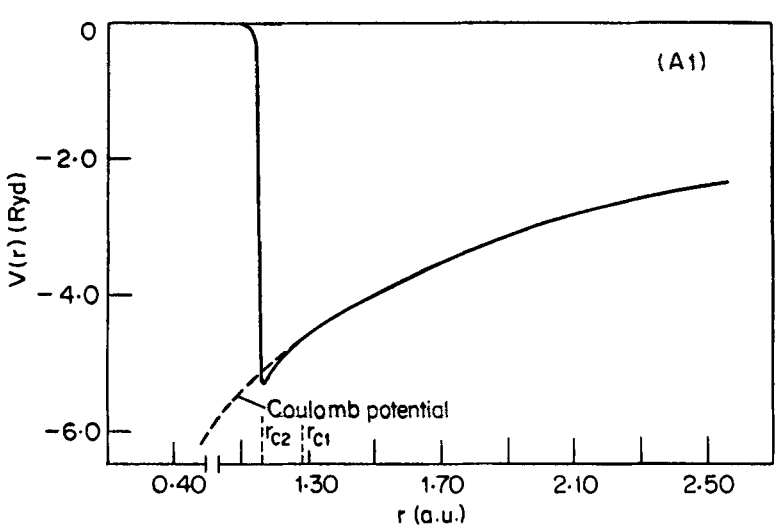

Figure 1. Curve showing the potential in r-space for Al (r_{c1} = 1·2805 a.u and r_{c2} = 1·1600 a.u.). Dotted portion indicates the extention of the Coulomb potential.

sidered the correlation energy in the form suggested by Pines (1963). The second term is the non-Coulomb part of the first order pseudopotential energy and is given by (according to the present model) $2\pi Z^2 e^2 r_{c1}^2/\Omega$. It may be pointed out here that the first order energy depends only on the parameter r_{c1} of the modified pseudopotential. The third term in (5) is the electrostatic energy of an array of point ions in a uniform electron gas and has been evaluated by Fuchs (1935). The last term is the band structure energy and is given by

$$E_B = -\sum_{\mathbf{G}}{}' \frac{\Omega\, \mathbf{G}^2}{8\pi e^2} |V(G)|^2 \frac{\epsilon(G)-1}{\epsilon(G)}$$

$$= -\sum_{\mathbf{G}}{}' \frac{2\pi Z^2 e^2}{\Omega\, \mathbf{G}^2} \cos^2 G r_c(G) \frac{\epsilon(G)-1}{\epsilon(G)} = \sum_{\mathbf{G}}{}' F_G, \tag{6}$$

where $\mathbf{G}$ is a reciprocal lattice vector and $\epsilon(G)$ is the dielectric function. It may be noted that the band structure energy given by (6) will almost entirely depend on the parameter r_{c2} as the lowest value of the reciprocal lattice vector is about hundred times larger than q_0. Thus the first and second order pseudopotential energies are controlled by the two different parameters r_{c1} and r_{c2} respectively. This in fact justifies the arbitrary procedure adopted by Price *et al* (1970) and points to the fact that the present modification is a natural extension of the Ashcroft pseudopotential that will explain both the static and dynamic properties of metals.

In order to account for the exchange and correlation between the conduction electrons, a large number of dielectric functions have been proposed and almost all of them can be reduced to the form

$$\epsilon(q) = 1 + \frac{\epsilon_H(q) - 1}{1 - f(q)(\epsilon_H(q) - 1)}, \tag{7}$$

where $\epsilon_H(q)$ is the Hartree dielectric function and $f(q)$ accounts for the correction due to exchange and correlation between the conduction electrons. A number of different approximate expressions for the function $f(q)$ have been proposed by Sham (1965), Kleinman (1967), Langreth (1969), Shaw and Pynn (1969), Singwi *et al* (1970), Geldart and Taylor (1970), Toigo and Woodruff (1970), Vashishta and Singwi (1972) and Taylor (1978). In the present calculation we have used the dielectric function proposed by Taylor (1978), because it can be represented by a simple analytical formula and exactly satisfies the compressibility sum rule, which is essential in order that the dielectric function correctly accounts for the change in the exchange and correlation energy due to the fluctuation of the electron gas density. In order to estimate the role of the dielectric function on the different properties of the solid we have repeated the calculation with the dielectric function proposed by Vashishta and Singwi (1972), which also closely satisfies the compressibility sum rule.

Starting from the energy expression given by (5) we have calculated the second order elastic constants and their pressure derivatives by the method of homogeneous deformation following the procedure outlined by Sen *et al* (1980). We have also obtained the equation of state of the crystal in a straightforward way.

4. Phonon frequencies

Phonon frequencies of metals depend on the effective interaction between ions which is a sum of the direct Coulomb interaction between the ions immersed in a uniform compensating negative background and the ion-electron-ion interaction arising from the screening of the ionic motion by the conduction electrons. The contribution of the first term to the dynamical matrix has been evaluated by Vosko *et al* (1965). The contribution of the second term to the dynamical matrix is given by

$$D_{\alpha\beta}(\mathbf{K}) = 2\Big[\sum_{\mathbf{G}} F_{|\mathbf{G}+\mathbf{K}|}(\mathbf{G}+\mathbf{K})_\alpha (\mathbf{G}+\mathbf{K})_\beta - \sum_{\mathbf{G}}{}' F_G\, G_\alpha\, G_\beta\Big], \qquad (8)$$

where F_G is the energy-wave-number characteristic and is defined by equation (6). Once the dynamical matrix is evaluated, the phonon frequencies can be calculated in a straightforward manner.

5. Results and discussions

The present model is used to make a comprehensive unified study of Al. The model contains two adjustable parameters r_{c1} and r_{c2}. As the pseudopotential parameters enter into the dynamical matrix through the band structure energy which depends only on r_{c2}, we adjust the parameter r_{c2} so that best agreement is obtained in the phonon dispersion. Next, using that value of r_{c2}, the parameter r_{c1} is adjusted to satisfy the equilibrium condition $\partial U/\partial\Omega\,|_{\Omega=\tilde{\Omega}} = 0$ exactly ($\tilde{\Omega}$ is the harmonic value of Ω). The fact that the present model parameters r_{c1} and r_{c2} are consistent with the equilibrium condition at zero pressure is also apparent from our calculated results of the equation of state (figure 3). The calculated properties include cohesive energy, equilibrium lattice constant, second order elastic constants and their pressure derivatives, equation of state and phonon frequencies along the symmetry directions. The calculated static properties along with the experimental results are shown in table 1.

It is seen from the table that the calculated cohesive energy according to the present model agrees within 0·5% with the experimental values. For the second order elastic constants, the picture that has emerged through the unified study indicates that there is a genuine problem here. For C_{11} and C_{44}, agreement between the calculated and the experimental values is reasonable for Taylor's dielectric function, but for C_{12} the discrepancy is very high (about 36%) for both the Taylor and the Vashistha-Singwi dielectric functions. Use of the Vashishta-Singwi dielectric function improves the agreement of C_{11} but impairs the agreement of C_{44} considerably.

We have also calculated the elastic constants of Al using the empty-core Ashcroft pseudopotential coupled with Taylor's dielectric function. The lone parameter r_c is determined from the equilibrium condition. The results of such a calculation are shown in table 1. Here the discrepancy is so high that even the order of magnitude of C_{44} does not agree with the experimental results. Kachhava (1973) used Ashcroft's pseudopotential to calculate phonon frequencies and the second order elastic constants of Al. He confined himself upto the second order perturbation in electron-ion pseudopotential and calculated the elastic constants by the method of long waves.

Table 1. Model parameters and calculated static properties of Al. Experimental values which are within parenthesis are extrapolated harmonic values.

Model Pseudopotential	Dielectric function	Model parameters a.u.	Crystal energy Ryd/atom	Equilibrium lattice constant a.u.	Elastic constants in 10^{12} dyn/cm^2			Pressure derivatives of elastic constants		
					C_{11}	C_{12}	C_{44}	$\frac{dC_{11}}{dp}$	$\frac{dC_{12}}{dp}$	$\frac{dC_{44}}{dp}$
Ashcroft	Taylor	$r_c = 1{\cdot}6166$	$-4{\cdot}1287$	7·5811	5·158	2·167	3·060	5·564	2·837	3·381
Modified Ashcroft	Taylor	$r_{c1} = 1{\cdot}2805$ $r_{c2} = 1{\cdot}1600$	$-4{\cdot}1230$	7·5811	1·051	0·406	0·323	8·144	2·719	3·972
Modified Ashcroft	Vashishta-Singwi	$r_{c1} = 1{\cdot}2608$ $r_{c2} = 1{\cdot}1500$	$-4{\cdot}1483$	7·5811	1·081	0·427	0·433	7·407	2·596	4·408
Experimental	—	—	$-4{\cdot}1420$ (a)	(7·5811) (b)	(1·199) (c)	(0·654) (c)	(0·337) (c)	7·350 ±0·230 (d)	2·450 ±0·160 (d)	3·100 ±0·120 (d)

(a) Handbook of Chemistry and Physics (1975), (b) Sutton (1953), (c) Gerlich and Fisher (1969) (d) Thomas (1968)

But, as pointed out by Bertoni *et al* (1974), one has to include the effects of the third and fourth order perturbation terms while calculating the elastic constants by the method of long waves.

Thus the values of elastic constants obtained by Kachhava are wrong. Again the value of r_c with which he got good agreement for the phonon frequencies will not reproduce the cohesive energy of the metal in question and will also not satisfy the equilibrium condition.

The problem concerning the elastic property of Al, surprisingly enough, seems to be common to all the existing pseudopotential calculations, either local or non-local. Gupta and Tripathi (1970) using Harrison's (1965) two-parameter model potential combined with some arbitrary cut-off procedure (Animalu and Heine 1965) obtained good results for the phonon frequencies and binding energy, but their calculated compressibility was too low with respect to the experimental value. Suzuki (1971) used the local form of Heine-Abarenkov (1964) potential in conjunction with the Hartree and the Hubbard-Sham (Hubbard 1957; Sham 1965) screening functions to calculate the second and third order elastic constants of Al. Here, except for C_{11}, the agreement between the calculated second order elastic constants and the corresponding experimental values is very poor. Recently Sarkar and Sen (1981) have also employed the Heine-Abarenkov model potential to make a unified study of Al. They have used both the dielectric functions of Taylor (1978) and Vashishta-Singwi (1972). Discrepancies in their calculated values of C_{11}, C_{12} and C_{44} (using Taylor's dielectric function) are 23%, 20% and 22% respectively. Use of Vashishta-Singwi dielectric function slightly improves the situation.

Hafner (1975) has attempted a unified study of static, dynamic and electronic properties of Al by incorporating the valence-core exchange and correlation effects in the framework of Harrison *ab-initio*-pseudopotential theory. He used an improved valence-core exchange potential containing two parameters. He has not calculated the individual elastic constants. For bulk-modulus which he has calculated the discrepancy is about 22%. For the other properties, the agreement with the experimental results is more or less reasonable. But the major defect in his calculation is that there is a discrepancy of 4% in his calculated zero-pressure lattice constant—this partly destroys the significance of the entire calculation.

The above calculations are based on second order perturbation in electron-ion pseudopotential. Inclusion of the third order perturbation terms does not lead to any improvement in the second order elastic constants of Al. In the calculations of Bertoni *et al* (1974), the discrepancy between the theoretical and the experimental values of C_{12} was about 46%. Brovman and Kagan (1974) carried out a unified study of lattice mechanical properties of some simple metals including Al. For Al, their calculated values of second order elastic constants, including the third order perturbation term, show a maximum discrepancy of about 27% in C_{12}.

The above facts suggest that at present a genuine difficulty exists in the calculation of second order elastic constants of Al, which has also been stressed by Sarkar and Sen (1981). In most of the calculations it is found that the agreement between the calculated and the experimental phonon frequencies is reasonably good. It appears that there is some interaction missing in all the investigations so far made in the framework of pseudopotential theories. Except dC_{44}/dp, the agreement for pressure derivatives of elastic constants is more or less reasonable when the present model is combined with the Taylor dielectric function. Using the Vashishta-Singwi dielectric

function the agreement of dC_{11}/dp and dC_{12}/dp improves (the agreement with the experimental values is almost exact), but the discrepancy of dC_{44}/dp increases appreciably. One interesting point to be noted here is that the agreement between the experimental and the theoretical values of pressure derivatives of elastic constants calculated on the basis of Ashcroft's (with the Taylor dielectric function) pseudopotential is far better than that of the elastic constants using the same model.

The equation of state (at $T = 0$) obtained with the present model gives good agreement with the experimental results. The results are shown in figure 3. The present pseudopotential coupled with the Vashishta-Singwi dielectric function gives better agreement.

Phonon frequencies along the symmetry directions calculated on the basis of the present model are displayed in figure 2. The overall agreement between the theoretical and the experimental values of Stedman and Nilson (1966) is good (Vashishta-Singwi dielectric function gives a slightly better result) for both the dielectric functions. For Taylor's dielectric function, phonon frequencies along [110] T_1 mode become slightly greater than the corresponding values along [110] T_2 mode for low values of **q**. This is in contrast to the experimental results. This defect disappears when calculations are made with the Vashishta-Singwi dielectric function. Thus, it appears that dielectric

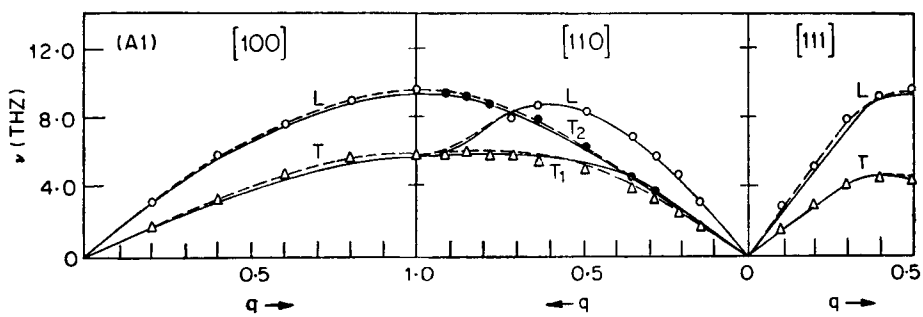

Figure 2. Phonon dispersion curve for Al at 80°K. Experimental points which are taken from Stedman and Nilson (1966) are indicated by O for longitudinal branches, △ and ● for transverse branches, ——— curve present model + Taylor's dielectric function and ..... curve present model + Vashishta-Singwi dielectric function.

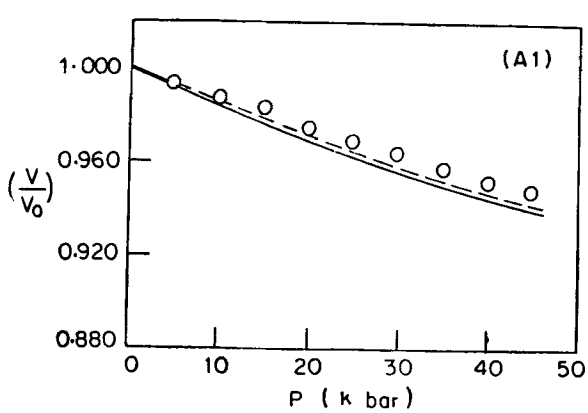

Figure 3. Equation of state (at $T = 0$) for Al. Experimental points (indicated by O) are taken from Vaidya and Kennedy (1970); ——— curve present model + Taylor's dielectric function; and ..... curve present model + Vashishta-Singwi dielectric function.

function plays an important role in reproducing the fine structure of phonon dispersion curves of metals.

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