UNIFIED STUDY OF ALKALI METALS ON PSEUDOPOTENTIAL MODELS. I

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A detailed calculation with the Ashcroft pseudopotential applied in a consistent way for the whole alkali metal group (except Cs), is worked out as a part of the unified study of metals in a pseudopotential frame-work. To facilitate the calculation of elastic constants and their pressure derivatives, a new homogeneous deformation theory has been developed and discussed in some detail giving explicit final expressions. The single parameter of the model potential is determined from the equilibrium condition. Most of the static properties are found to be in fairly good agreement with experiment. In the pressure derivative of C_{44}, however, the discrepancy is large and it is of the order of twenty per cent. But the major failure of the model is revealed in the dispersion curves where the maximum disagreement with experiment is as high as forty percent near the zone boundaries. The reason for this failure is examined.

1. Introduction

The study of metals on the basis of the pseudopotential theory has made spectacular progress during the last ten years. This theory is particularly important for those properties of metals which depend on the existence of an effective potential energy which is a function of the ionic co-ordinates and the mean atomic volume of the crystal. These properties include both the dynamic and static properties. In recent years pure phenomenological studies of earlier years have been more or less completely replaced by pseudopotential theories. The success of these theories in specific problems has been so encouraging that one feels that comprehensive unified studies of metals must now be very fruitful. Unfortunately such studies are very rare, even with a simple local pseudopotential model such as that of Ashcroft (1966). There has been a large number of studies of the properties of alkali metals on the Ashcroft model but none of them aims at a unified study. Ashcroft potential contains only one parameter, but Ashcroft (1967) himself and some other authors (1970) used two different values for the same parameter in the first and the second order

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energy expressions respectively in their calculations. This makes the model inconsistent. Dunn et al. (1974) used a consistent one parameter Ashcroft model, determined the value of the parameter from the equilibrium condition and calculated a few of the static properties only. It is quite obvious that such studies do not bring out clearly the degree of reliability and the inadequacy of a pseudopotential properly.

Brovman and Kagan (1974), to our knowledge, are the only authors who have attempted a unified study for some of the metals. They used a local form of the Heine–Abarenkov potential with a tail end cut off so that altogether it has three parameters. Of the alkali metals they studied only sodium. They have also discussed in detail some of the difficulties of such a study. One of the main difficulties is the calculation of elastic constants. Earlier Suzuki et al. (1968) and Wallace (1969) had developed methods of homogeneous deformation (h.d.) after Fuchs (1935) for calculating elastic constants. But their method of calculating first the Fuchs elastic constants and then converting them to Brugger elastic constants is rather cumbrous. Instead we use a straightforward method of h.d. (1978), discussed briefly in Section 2, which is much simpler than the previous h.d. methods or compared to the tedious long wave method that has to include the third and fourth order terms in the energy expression.

In Section 3, we undertake a unified study of the properties of four alkali metals Li, Na, K and Rb, on the basis of one parameter Ashcroft pseudopotential. There parameter is determined from the equilibrium condition. The results are discussed in Section 4. Our conclusion is that Ashcroft model is unable to give good results for both the static and dynamic properties simultaneously. The cause of this inadequacy has been discussed.

2. Homogeneous deformation theory for elastic constants

According to the second order pseudopotential theory, the energy/atom for a perfect simple metallic lattice is given by (V = Volume per ion),

$$E = E_1(V)+E_2(es)+E_3(bs), \tag{1}$$

where E_1 is a purely volume dependent energy and is given for monovalent metals by

$$E_1 = \frac{5.7427}{V^{2/3}} - \frac{1.4766}{V^{1/3}} -(0.1199-0.0103 \ln V)+\omega_0^{nc} \tag{2}$$

ω_0^{nc} being the non-Coulomb part of the first order pseudopotential energy.

The electrostatic energy E_2 of the positively charged ionic lattice immersed in a uniform distribution of negative charge is, according to Fuchs (1935) (in a.u.)

$$E_2 = c \sum_l{}' H(cr_l)+ \frac{1}{\pi V} \sum_G{}' \frac{e^{-(\pi^2G^2/c^2)}}{G^2} - \frac{2c}{\pi} - \frac{\pi}{c^2V}, \tag{3}$$

where

$$H(x) = \frac{2}{\sqrt{\pi}} \frac{1}{x} \int_x^\infty e^{-\kappa^2} d\kappa,$$

and c is an arbitrary constant having the dimension of cm^{-1}, G is any reciprocal lattice vector.

The band structure energy E_3 may be written as (in a.u.),

$$E_3 = \sum_G{}' \frac{VG^2}{16\pi} |\omega_G|^2 \frac{1-\varepsilon(V, G)}{\varepsilon(V, G)}, \tag{4}$$

where ω_G is the bare pseudopotential matrix element and $\varepsilon(V, G)$ is the Hartree dielectric function.

Thus the total energy per unit cell has three different types of contribution, 1) purely volume dependent, 2) two body central interaction in direct space and 3) volume dependent two body central interaction in reciprocal lattice space. Since the expression for the total energy is valid for any primitive lattice, one can differentiate it with respect to homogeneous deformations and calculate the contribution to Brugger elastic constants from each term in the following way.

A. Volume dependent energy

The uniform electron gas energy E_1 and the term involving π/c^2V in E_2 depend only on volume. By expanding this energy $(E_1 - \pi/c^2V) = \mathscr{E}_1$ in terms of the Lagrangian strain tensor, one can easily calculate the contribution to elastic constants (see Das et al. (1977)) and these are, for a cubic crystal,

$$C_{11}^V = k_1 + p_1, \quad C_{12}^V = k_1 - p_1, \quad C_{44}^V = p_1, \tag{5}$$

where $k_1 = V \left.\frac{d^2\mathscr{E}_1}{dV^2}\right|_{V_0}$, $p_1 = -\left.\frac{d\mathscr{E}_1}{dV}\right|_{V_0}$, V_0 = equilibrium value of V

B. Two body central interaction in direct space

Let us write the energy per atom as

$$\mathscr{E}_2 = \tfrac{1}{2}\sum_l{}' \phi_1(r_l), \tag{6}$$

where r_l stands for r_{0l}. We can expand this energy in powers of $\mathscr{S}$, and from the second order terms, we get the contribution to the elastic constants. The results are

$$C_{11} = \frac{1}{2V_0}\sum_l{}' D_l^2\phi_1(r_{l1})^4, \quad C_{12} = C_{44} = \frac{1}{2V_0}\sum_l{}' D_l^2\phi_1(r_{l1})^2(r_{l2})^2, \tag{7}$$

where $D_l = \frac{1}{r_l}\frac{d}{dr_l}$.

C. Volume dependent two body central interaction in reciprocal lattice space

We may write this part of the energy/atom in the form

$$\mathscr{E}_3 = \tfrac{1}{2}\sum_V{}' \phi_2(V, G). \tag{8}$$

When the direct lattice is subjected to a Lagrangian strain $\mathscr{S}$, it induces a Lagrangian strain $\mathscr{C}$ in the reciprocal space, given by

$$\mathscr{C} = -\mathscr{S} + 2\mathscr{S}^2.$$

Contributions to elastic constants obtained in similar way, are

$$C_{11} = \frac{1}{2V_0}\sum_G{}' \left(D_G^2\phi_2 G_1^4 - 2V_0 D_G \frac{\partial\phi_2}{\partial V}\bigg|_{V_0} G_1^2 + 4D_G\phi_2 G_1^2 \right) + k_2 + p_2,$$

$$C_{12} = \frac{1}{2V_0}\sum_G{}' \left(D_G^2\phi_2 G_1^2 G_2^2 - V_0 D_G \frac{\partial\phi_2}{\partial V}\bigg|_{V_0} (G_1^2 + G_2^2) \right) + k_2 - p_2,$$

$$C_{44} = \frac{1}{2V_0}\sum_G{}' (D_G^2\phi_2 G_1^2 G_2^2 + D_G\phi_2(G_1^2 + G_2^2)) + p_2, \tag{9}$$

where the operator $D_G = \dfrac{1}{G}\dfrac{\partial}{\partial G}$, $k_2 = V_0 \dfrac{\partial^2\mathscr{E}_3}{\partial V^2}\bigg|_{V_0}$ and $p_2 = -\dfrac{\partial\mathscr{E}_3}{\partial V}\bigg|_{V_0}$. Expressions for the higher order elastic constants may easily be obtained collecting the corresponding higher order terms in the energy expansion.

3. *Results and discussion*

The pseudopotential parameter r_c is determined from the equilibrium condition $(\partial U/\partial V)|_{V_0} = 0$, assuming zero pressure. Dunn (1975) also used the same procedure and hence our values of r_c are the same as those of Dunn, which are 1.416, 1.940, 2.634 and 2.872 and a.u. for Li, Na, K and Rb respectively. The results of calculation of the various properties for the four alkali metals are given in Table I and in Fig. 1, and compared with experimental results.

Using the equilibrium lattice constant as the only input data we have studied the static properties like cohesion, the second order elastic constants and their pressure derivatives and the dispersion curves along the symmetry directions. The cohesive energy agrees excellently with experiment. The maximum discrepancy of about five per cent occurs for Li. For the three other metals the agreement is almost perfect. The elastic constants agree within five percent for Li and Na. For K and Rb the discrepancy varies from fifteen to twenty percent and the calculated values are always higher. For pressure derivatives, the agreement for dC_{11}/dp and dC_{12}/dp is surprisingly good, the discrepancy is less than

TABLE I

Static properties evaluated for alkali metals. The values in the parenthesis are experimental (harmonic) values (β = bulk modulus)

Crystals	Crystal energy	Second order elastic constants			Pressure derivatives of second order elastic constants			
	U (Ryd)	C_{11} (10^{12} dynes per cm^2)	C_{12} (10^{12} dynes per cm^2)	C_{44} (10^{12} dynes per cm^2)	$\frac{dC_{11}}{dp}$	$\frac{dC_{12}}{dp}$	$\frac{dC_{44}}{dp}$	$\frac{d\beta}{dp}$
Li	0.543 (0.517) [a]	0.157 (0.157) [b]	0.129 (0.133) [b]	0.122 (0.117) [b]	4.897	2.387	2.632 (2.17) [c]	3.224 (3.33) [g]
Na	0.461 (0.460) [a]	0.091 (0.086) [b]	0.074 (0.072) [b]	0.069 (0.063) [b]	5.198 (5.17) [d]	2.700 (2.635) [d]	2.433 (2.69) [d]	3.533 (3.48) [d] (3.69) [g]
K	0.388 (0.388) [a]	0.050 (0.043) [b]	0.041 (0.035) [b]	0.034 (0.029) [b]	5.123 (5.31) [e]	2.746 (2.808) [e]	2.103 (2.62) [e]	3.538 (3.642) [e] (3.65) [g]
Rb	0.369 (0.370) [a]	0.042 (0.035) [b]	0.034 (0.030) [b]	0.027 (0.022) [b]	4.814 (4.96) [f]	2.475 (2.502) [f]	1.991 (2.48) [f]	3.255 (3.321) [f] (3.37) [g]

[a] Kittel (1976), [b] Simmons (1971), [c] Jain (1961), [d] Martinson (1969), [e] Smith (1965), [f] Pauer (1968), [g] Vaidya (1971).

four percent in all cases. But for dC_{44}/dp the discrepancies are much larger and vary from ten per cent (for Na) to about twenty per cent (for Li, K and Rb).

In the case of static properties, it is found that the first order perturbation energy plays a very important role and is more significant than the band structure energy. The overall satisfactory agreement of static property achieved by the Ashcroft model indicates that the estimate of the first order energy in this model is more or less correct.

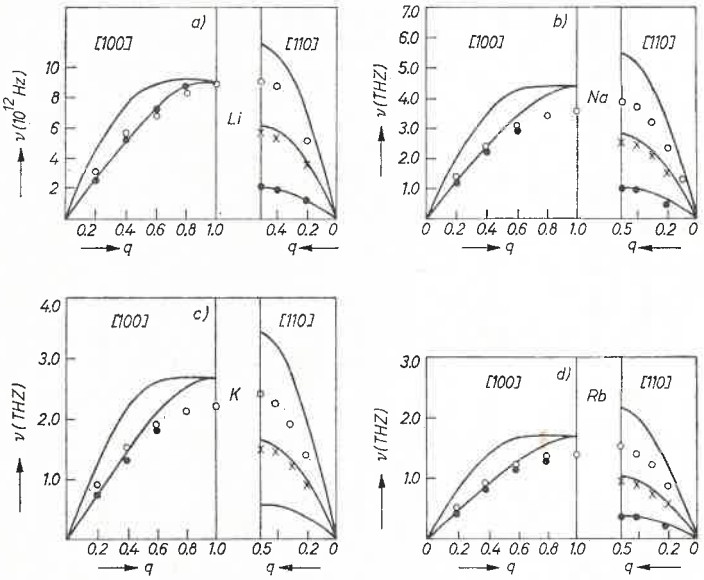

Fig. 1a). Phonon dispersion curves in (100) and (110) directions for Li at 90 K. The experimental points which are taken from Smith et al. (1968) are indicated by o for longitudinal branches and × and ● for transverse branches. b). Phonon dispersion curves for Na. Experimental points are taken from Woods et al. (1962). c). Phonon dispersion curves at 9 K for K. The experimental points are taken from Cowley et al (1966). d). Phonon dispersion curves for Rb at 120 K. The experimental points are taken from Copley et al. (1973)

In the case of dispersion curves, however, the results are very disappointing. In Fig. 1 the results are shown for (100) and (110) directions only. For the (111) direction also, the disagreement is similar. A fair agreement in dispersion can only be achieved with widely different r_c values impairing seriously the equilibrium condition and all other agreements achieved in static properties. It may be pointed out that the large discrepancies near the zone boundary of the (100) direction has nothing to do with the omission of exchange and correlation correction in the dielectric function. Also the inclusion of third and fourth order terms in the dynamical matrix is of little consequence considering the large overall disagreement.

Earlier Price et al. (1970), while studying phonon dispersion, used a widely different values for the parameters for alkali metals. These values of the parameters could not satisfy the equilibrium condition, nor did they reproduce other static properties in agreement with experiments. So the authors had to parametrize the first order energy separately, making the model inconsistent.

Since the dispersion curves are mainly determined by the band structure energy, the failure of the Ashcroft model here probably indicates that the estimate of the band structure energy in this model is seriously in error. In the two-parameter Heine-Abarenkov potential the first order energy is given by $4\pi r_c^2(1+\frac{2}{3}U)/V_0$ which has the same form as in the Ashcroft model. By a suitable choice of the parameter $r_c^2(1+2U_{1/3})$ the good agreement of static properties can also be obtained in Heine-Abarenkov model. But the second order energy in this model is entirely different from that in Ashcroft model. One would therefore expect that by a suitable choice of the extra parameter U_1, a much better agreement can be achieved in the dispersion curves. This is exactly what has been found by Brovman and Kagan (1974) in their study of Na with a Heine–Abarenkov pseudopotential. A unified study of the properties of all the alkali metals on the basis of this potential is in progress and will be reported later.

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REFERENCES

Ashcroft, N. W., *Phys. Lett.* **23**, 48 (1966).
Ashcroft, N. W., Langreth, D. E., *Phys. Rev.* **155**, 682 (1967).
Brovman, E. G., Kagan, Yu. M., *Dynamical Properties of Solids*, Vol. 1, Ed. G. K. Horton and A. A. Maradudin, North Holland Publ. Co. 1974, p. 283.
Copley, J. R. D, Brockhouse, B. N., *Can. J. Phys.* **51**, 657 (1973).
Cowley, R. A., Woods, A. D. B., Dolling, G., *Phys. Rev.* **150**, 487 (1966).
Das, S. K., Roy, D., Sengupta, S., *Pramana* **8**, 117 (1977).
Dunn, K. J., Ruoff, A. L., *Phys. Rev.* **B10**, 2271 (1974).
Dunn, K. J., *Phys. Rev.* **B12**, 3497 (1975).
Fuchs, K., *Proc. R. Soc.* (London) **A151**, 585 (1935).
Harrison, W. A., *Pseudopotentials in the Theory of Metals*, Benjamin, New York 1966.
Jain, A. L., *Phys. Rev.* **123**, 1234 (1961).
Kittel, C., *Introduction to Solid State Physics*, 5th Ed., Wiley, London 1976, p. 74.
Martinson, R. H., *Phys. Rev.* **178**, 902 (1969).
Pauer, L. A., O. N. R. Technical Report 11, Proj. N. R017–309, 1968,
Pines, D., *Elementary Excitations in Solids*, Benjamin, New York 1963.
Price, D. L., Singwi, K. S., Tosi, M. P., *Phys. Rev.* **B2**, 2983 (1970).
Sen, D., Sarkar, S. K., Das, S. K., Roy, D., Sengupta, S., Proc. Nuclear Phys. and Solid State Phys. Symp., India, 1978.
Simmons, G., Wang, H., *Temperature Variation of Elastic Constant and Calculated Aggregate Properties*, M. I. T. 1971.
Smith, H. G., Dolling, G., Nicklow, R. M., Vijayaraghavan, P. R., Wilkinson, M. K., Proc. Conf. on Inelastic Neutron Scattering, Vienna International Atomic Energy Agency 1968, p. 149.
Smith, P. A., Smith, C. S., *J. Phys. Chem. Solids* **26**, 279 (1965).
Suzuki, T., Granato, A. V., Thomas, J. F., *Phys. Rev.* **175**, 766 (1968).
Vaidya, S. N., Geting, I. C., Kennedy, G. C., *J. Phys. Chem. Solids* **32**, 2545 (1971).
Woods, A. D. B., Brockhouse, B. N., March, R. H., Stewart, A. T., Bowers, R., *Phys. Rev.* **128**, 1112 (1962).