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Pseudopotential study of alkali metals: Unified approach

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A comprehensive unified calculation of both the lattice static and dynamical properties for the whole alkali-metal group (except Cs) in the pseudopotential framework is presented. Both Ashcroft and Heine-Abarenkov pseudopotentials combined with different forms of static dielectric functions have been used to calculate cohesive energy, equilibrium lattice parameters, second-order elastic constants, pressure derivatives of second-order elastic constants, and phonon dispersion in the symmetry directions for the four alkali metals Li, Na, K, and Rb. The mode Grüneisen parameters have been calculated for Na and K, for which experimental data are available. It is found that the two-parameter Heine-Abarenkov potential in conjunction with a dielectric function of a very simple form proposed recently by Taylor yields satisfactory results. The Heine-Abarenkov potential, coupled with the self-consistent dielectric function of Vashishta and Singwi, gives similar results. This agreement is justified from a comparison of the correction factor introduced by the two dielectric functions, over the screening function of Lindhard.

I. INTRODUCTION

The vast literature on lattice dynamical studies of metals abounds with examples in which for the same crystal, and the same model, various authors in their calculations of different properties use different values of the model parameters. This is not a meaningful procedure. No significant conclusion about the strength and weakness of a model can be made from the results of such calculations. On the other hand, one may put a model to a stringent empirical test by calculating a large number of different properties with the same set of parameters. Any artificiality in the values of the parameters or shortcomings in the model itself are bound to show up as a strong discrepancy in one or more properties. Thus, through unified studies alone, both the strength and limitations of a model come out clearly. Brovman and Kagan[1] have pointed out that a unified study is important for checking even a microscopic theory.

The development of pseudopotential theory into a practical computational tool has resulted in a breakthrough in the studies of properties of metals, and during the last ten years or so, such studies have made a tremendous impact. But, in spite of their impressive success in solving specific problems, attempts at comprehensive unified studies are surprisingly rare, even with local pseudopotential models.

The first attempt at a unified study of metals, so far as we know, appears to be that of Brovman *et al.*[1] who used a local form of the Heine-Abarenkov potential for a unified study of some simple metals. Krasko and Gurskii[2-4] also have made some attempts, though in a somewhat scattered manner, at a unified calculation of properties of some metals using a two-parameter model pseudopotential proposed by themselves.

Recently Sarker *et al.*[5] have reported a unified calculation using the Ashcroft pseudopotential in a consistent way, for the whole alkali-metal group. They obtained fair agreement for static properties. But in the case of phonon dispersion, the maximum disagreement with experiment was more than 40%, which clearly indicates the inadequacy of the Ashcroft model for a comprehensive unified study. In the process, they have also pointed out the inconsistency of an earlier calculation made by Price *et al.*,[6] who in effect used three adjustable parameters in their calculation of some properties of alkali metals.

In the present work, we wish to undertake a unified study of the properties of the alkali metals on the basis of the local form of the two-parameter Heine-Abarenkov pseudopotential. The model has been used in conjunction with dielectric functions proposed by Lindhard,[7] Vashishta and Singwi,[8] and Taylor.[9] Parameters used are best-fit parameters with the harmonic equilibrium condition satisfied exactly. Calculations with the Ashcroft potential have been repeated, but with a better dielectric function. The results are then critically compared with those obtained by Sarkar *et al.*[5]

Elastic properties have been calculated using the homogeneous deformation theory developed by Sen *et al.*[10] Earlier Suzuki *et al.*[11] and Wallace[12] had developed methods of homogeneous deformation after Fuchs.[13] But their methods of calculating first the Fuchs elastic constants and then converting them to Brugger elastic constants is rather cumbersome. The long-wave method, on the other hand, is very tedious and suffers from the defect that the correct values are not obtained unless one uses the third- and fourth-order-perturbation terms in the dynamical matrices. We have used the straightforward method developed by Sen *et al.*[10] by which second- and third-order elastic constants and their pressure derivatives can be calculated in a simple and elegant way.

On the basis of the calculations made, our conclusions are as follows. (i) The Ashcroft model does not give reasonable results for both the static and dynamic properties simultaneously even when better dielectric functions are used (surprisingly enough, a dielectric function better than Lindhard's coupled with the Ashcroft potential worsens the results considerably). (ii) The Heine-Abarenkov potential combined with the Vashishta-Singwi or Taylor dielectric function can yield quite satisfactory results for lattice mechanical properties for the entire alkali-metal group. (iii) Conduction-electron exchange and correlation effects are sufficiently strong so that the use of a sound dielectric function satisfying the compressibility sum rule is very important.

In Sec. II, a brief outline of the theory is given. In Sec. III, dielectric screening is briefly discussed. Section IV describes the results obtained and includes a critical discussion of the results.

II. THEORY

For simple monovalent metals, the second-order pseudopotential theory expresses the total energy per unit cell for a perfect lattice as

$$U=E_1(v)+E_2(\mathrm{es})+E_3(\mathrm{bs})\,, \tag{1}$$

where v is the volume per unit cell. $E_1(v)$ is the purely volume-dependent energy consisting of the kinetic, exchange, correlation, and the non-Coulomb part of the first-order pseudopotential energy and is given by (in a. u.)

$$E_1(v)=\frac{5.7427}{v^{2/3}}-\frac{1.4766}{v^{1/3}}-E_{\mathrm{corr}}+\frac{1}{r_s^3}(3+2u)r_c^2\,. \tag{2}$$

Here, E_{corr} is the correlation energy, and u and r_c are the two parameters of the Heine-Abarenkov potential,

$$V(r)=\begin{cases}\dfrac{ze^2u}{r_c}\,, & r\leq r_c\\[2ex] -\dfrac{ze^2}{r}\,, & r>r_c\,.\end{cases} \tag{3}$$

The second term in Eq. (1), $E_2(\mathrm{es})$, is the electrostatic energy of the positively charged ionic lattice immersed in a uniform distribution of negative charge and is given by, according to Fuchs,[12]

$$E_2(\mathrm{es})=c\sum_l{}'\,H(cr_l)+\frac{1}{\pi v}\sum\frac{e^{-(\pi^2G^2/c^2)}}{G^2}-\frac{2c}{\sqrt{\pi}}-\frac{\pi}{c^2v}\,, \tag{4}$$

where

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

and c is an arbitrary constant having dimension cm^{-1}, $\vec{G}$ is a reciprocal lattice vector. The third term, $E_3(\mathrm{bs})$ is the band-structure energy given by

$$E_3(\mathrm{bs})=\sum_G{}'\,\frac{vG^2}{16\pi}|w_G|^2(\epsilon^{-1}-1)\,, \tag{5}$$

where $\epsilon=\epsilon(v,G)$ is the static electron-gas dielectric function, and w_G, the Fourier transform of the potential $V(r)$, is given by

$$w_G=-\frac{8\pi}{vG^2}\left((1+u)\cos Gr_c-u\frac{\sin Gr_c}{Gr_c}\right). \tag{6}$$

Thus the total energy per unit cell has three different types of contributions—(a) purely volume dependent, (b) two-body central interaction in the direct lattice space, and (c) volume-dependent two-body central interaction in reciprocal space.

The expression for total energy shown above is valid for any primitive lattice, and, following Sen *et al.*[10] one can easily calculate the elastic moduli and their pressure derivatives in a straightforward way by expanding the energy expression in terms of Lagrangian strain.

Phonon frequencies of simple metals are calculated from an effective interaction between ions which is the sum of direct Coulomb repulsion between ions immersed in a uniform compensating negative charge and 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 can be evaluated by Ewald's method (see Born and Huang,[14] Vosco *et al.*[15]). The contribution of the second term to the dynamical matrix, in the framework of the second-order perturbation theory, is given by

$$D_{\alpha\beta}(Q)=2\left(\sum_G F_{|G+Q|}(G+Q)_\alpha(G+Q)_\beta-\sum_G{}'\,F_GG_\alpha G_\beta\right), \tag{7}$$

where F_G is the energy-wave-number characteristic.

The repulsive interaction due to core-wave-function overlap is insignificant, at least for lighter alkali metals.[16] We have totally neglected this part though it may have some effects in the case of Rb.

The expressions for energy, elastic moduli, dynamical matrix, etc., for the Ashcroft potential, in which the well depth inside the core is zero, can be obtained by setting $u=0$ in the corresponding expressions for the Heine-Abarenkov potential.

III. DIELECTRIC SCREENING

The dielectric formulation of the many-body problem has been found to be very fruitful in studying the degenerate electron gas and the metallic properties which depend strongly on electron-electron interaction. Actually, the dielectric function has a central role in the calculation of properties of metals based on perturbation technique, and an accurate representation of this function is an important requirement for the calculation of fundamental properties of metals.

The simplest approximation to $\epsilon(q)$, the static dielectric function, which incorporates the Fermi statistics of the electron system, is the Lindhard dielectric function given by

$$\epsilon(q)=1+Q_0(q)\,, \tag{8}$$

where $Q_0(q)$ is the Lindhard expression for $(-4\pi e^2/q^2)$ times the susceptibility of the electron system. But this dielectric function totally neglects the conduction electron exchange and correlation effects.

Following Hubbard[17] a very large number of dielectric functions have been proposed in an attempt to absorb the exchange and correlation effects and almost all of them can be reduced to the form

$$\epsilon(q)=1+\frac{Q_0(q)}{1-f(q)Q_0(q)}\,, \tag{9}$$

where $f(q)$, the local-field correction, will be different for different forms of dielectric functions. Effectively, Eq. (9) introduces a correction factor $[1-f(q)Q_0(q)]^{-1}$ over the Lindhard value of $\epsilon(q)-1$.

In our calculations we have attached much importance to the use of a sound dielectric function. Prakash and Joshi[18] made exhaustive calculations in order to study the effects of dielectric functions on lattice dynamics of a simple metal, Na. They concluded that the dielectric functions developed in a fundamental way are better than those where some empirical factors are grafted. Up to recent times, amongst the fundamentally developed functions, those proposed by Geldart and Taylor,[19] Toigo and Woodruff,[20] and Vashishta and Singwi[8] are very keenly competing on fundamental grounds, as well as on consideration of their success when applied to the study of metallic properties. From them we have chosen $\epsilon(q)$ of Vashishta and Singwi $[\epsilon_{VS}(q)]$ because it satisfies the compressibility sum rule more closely than do the other two forms. This function, which is a modified form of an earlier self-consistent function developed by Singwi *et al.*,[21,22] also gives a physically acceptable pair-correlation function. The authors have further suggested an analytical formula for the local-field correction given by

$$f(q)=A[1-e^{-B(q/k_F)^2}]\,, \tag{10}$$

A, B being two constants for a given r_s. k_F is the Fermi wave vector. We have actually used this analytical form of $f(q)$ in our calculations using the Vashishta-Singwi screening function.

Recently, Taylor[9] has suggested a very simple analytical formula for $\epsilon(q)$ which satisfies the compressibility sum rule exactly and also has a good formal justification. He suggested an analytical formula for $f(q)$ of the form,

$$f(q)=q^2\phi(0)=q^2\left(1+\frac{0.1534}{\pi k_F}\right)\Big/4k_F^2\,, \tag{11}$$

where

$$\phi(0)=\lim_{q\to 0} f(q)/q^2\,.$$

The author has pointed out that using this value of $\phi[=\phi(0)]$ for all values of q is equivalent to the well-established Kohn-Sham[23] exchange and correlation approximation.

We have singled out the dielectric function proposed by Taylor $[\epsilon_T(q)]$ because both its simplicity and its initial success as reported by the author are quite appealing.

It is the usual practice to plot the so called "effective-interaction" function $f(q)/q^2$ in different approximations for a comparative study of their behaviors.[9,1] But it is found that dielectric functions with widely different effective-interaction curves yield almost similar results when applied to calculate metallic properties. We think it to be more appropriate to compare the "correction-factor" curves for different dielectric functions. Figure 1 shows the correction-factor curves corresponding to (a) the Vashishta-Singwi analytical form of $f(q)$, (b) numerical values of $f(q)$ given in their paper,[8] and (c) Taylor's $f(q)$. For the entire range of q, (b) and (c) are close to each other. Their separation at $q\to 0$ is a reminder of the fact that the Vashishta-Singwi dielectric function deviates slightly from the compressibility sum rule. On the other hand, the large separation of the curve corresponding to (a) from those corresponding to (b) and (c) near $q\to 0$ is due to the fact that the analytical form of the Vashishta-Singwi dielectric function deviates considerably from the compressibility sum rule, indicating that the extension of this form to very low q values is not advisable.

It may be pointed out here that the large-q behavior of Taylor's $f(q)$ given by Eq. (11) is quite obviously in serious error, because in the large-q limit, $f(q)$ is rigorously a constant. But if we

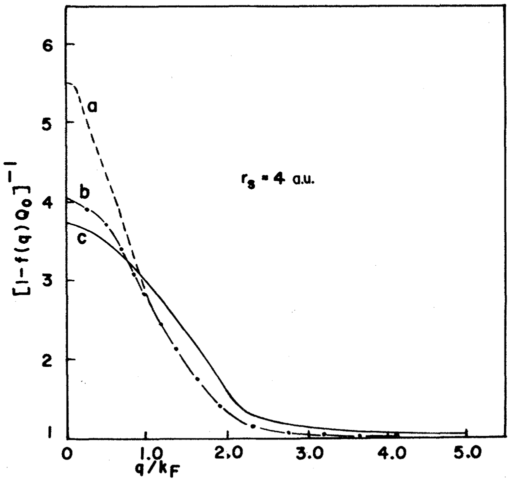

FIG. 1. Correction-factor curves corresponding to Vashishta-Singwi (chain curve), Taylor (full curve), and analytical form of Vashishta-Singwi (broken curve) dielectric functions. All curves are drawn for $r_s = 4$ a.u.

consider the value of $\epsilon(q) - 1$, then due to the rapid fall of $Q_0(q)$ ($\sim 1/q^4$), this serious error in $f(q)$ has only a mild effect in the large-q limit, and the correction factor falls to one with a slightly smaller rate compared to the VS correction factor, for which $f(q)$ has the right large-q behavior (see Fig. 1). Our investigation shows that this small difference is not of much consequence for the properties we have calculated. It may, however, be of considerable interest to examine if this difference will show up significantly in some physical properties of metals where the large-q part of the dielectric function plays an important role.

IV. RESULTS AND DISCUSSIONS

In our calculations, we have used both the two-parameter Heine-Abarenkov potential and the one-parameter Ashcroft potential. The Heine-Abarenkov potential has been used in conjunction with Lindhard, Vashishta-Singwi, and Taylor dielectric functions. The two parameters of the model are best-fit parameters with the equilibrium condition satisfied exactly. To suppress the tail-end oscillations arising out of the discontinuity in the potential, we used a sharp cutoff at a large-q value.

The Ashcroft potential combined with both Lindhard and Taylor dielectric functions has also been used to calculate the same metallic properties. The lone parameter of the model has been determined from the equilibrium condition.

The calculated properties include cohesive energy, equilibrium lattice constant, second-order elastic constants, pressure derivatives of second-order elastic constants, phonon dispersion along the symmetry directions, and mode Grüneisen parameters.

In all cases the equilibrium lattice constants were reproduced exactly. For cohesive energy, the agreement is excellent in all cases.

For the Heine-Abarenkov potential, the use of Vashishta-Singwi and Taylor dielectric functions generate almost the same overall agreement in all the static properties. In both cases the result is quite satisfactory. But for dc_{44}/dp there is a systematic discrepancy for all the four metals, the maximum being of the order of 20% for Li. The use of the Lindhard dielectric function worsens the overall agreement only slightly. The Ashcroft potential combined with the Lindhard dielectric function yields reasonably satisfactory results though definitely worse than those of the above calculations. But surprisingly enough, the use of a better dielectric function, such as that of Taylor, worsens the results beyond all expectations. This worsening is maximum in the case of Rb and minimum in the case of Li. Results of these calculations of static properties are shown in Tables I, II, III, and IV for Li, Na, K, and Rb, respectively.

In phonon dispersion, the Ashcroft and Lindhard combination produces quite disappointing results, the maximum discrepancy exceeding 40%. Again, as in the case of static properties, the use of the Ashcroft and Taylor combination increases the discrepancy, the maximum discrepancy shooting above 50%.

These facts indicate that the estimates of both the first-order energy and band-structure in this model are seriously in error, and the more or less satisfactory agreement for static properties produced by the Ashcroft-Lindhard combination appears to be fortuitous. It also proves decisively that the empty-core assumption in this model is too drastic even in the cases of monovalent simple metals.

Dispersion results improve considerably by employing the Heine-Abarenkov and Lindhard combination except in the case of Li, for which almost no improvement takes place. But the maximum improvement is more than 20% in the case of Na, 25% in the case of K, and 30% in the case of Rb.

Striking improvement of calculated results takes place with the use of Heine-Abarenkov and Vashishta-Singwi or the Heine-Abarenkov and Taylor combination. In both cases the overall agreement comes within 1 to 2 percent. The only failure of these combinations is in reproducing the crossing of L and T branches for Li along the ⟨100⟩ direction. The reproduction of this crossing probably necessitates the introduction of nonpairwise forces through the inclusion of third- and fourth-order terms in the dynamical matrix. Sarkar *et al.*[24]

TABLE I. Model parameters and calculated harmonic and experimental values of static properties of Li. Experimental values in the parentheses are harmonic values.

Model pseudo-potential	Dielectric function	Model parameters (a.u.)	Calculated properties								
			Crystal energy (Ry/atom)	Equilibrium lattice const. (a.u.)	C_{11} (10^{12} dyne /cm^2)	C_{12} (10^{12} dyne /cm^2)	C_{44} (10^{12} dyne /cm^2)	dC_{11}/dP	dC_{12}/dP	dC_{44}/dP	$d\beta/dP$
Ashcroft	Lindhard	$r_c = 1.4011$	−0.5470	6.5621	0.1539	0.1274	0.1233	5.046	2.388	2.678	3.274
Ashcroft	Taylor	$r_c = 1.4344$	−0.5429	6.5621	0.1610	0.1291	0.1336	5.292	2.494	2.798	3.274
Heine-Abarenkov	Lindhard	$r_c = 1.3973$ $u = +0.0333$	−0.5457	6.5621	0.1570	0.1284	0.1257	5.072	2.309	2.667	3.230
Heine-Abarenkov	Vashishta-Singwi	$r_c = 1.4958$ $u = -0.254$	−0.5480	6.5621	0.1532	0.1272	0.1191	4.949	2.373	2.676	3.232
Heine-Abarenkov	Taylor	$r_c = 1.5217$ $u = -0.296$	−0.5481	6.5621	0.1530	0.1272	0.1194	4.984	2.401	2.711	3.262
Experiments			(−0.517) (Ref. 34)	(6.5621) (Ref. 35)	(0.157) (Ref. 35)	(0.133) (Ref. 35)	(0.117) (Ref. 35)			(2.17) (Ref. 36)	(3.224) (Ref. 37)

TABLE II. Model parameters and calculated harmonic and experimental values of static properties of Na. Experimental values in the parentheses are harmonic values. (β = bulk modulus.)

Pseudo-potential	Dielectric function	Model parameters (a.u.)	Calculated properties								
			Crystal energy (Ry/atom)	Equilibrium lattice const. (a.u.)	C_{11} (10^{12} dyne /cm^2)	C_{12} (10^{12} dyne /cm^2)	C_{44} (10^{12} dyne /cm^2)	dC_{11}/dP	dC_{12}/dP	dC_{44}/dP	$d\beta/dP$
Ashcroft	Lindhard	$r_c = 1.9400$	−0.4617	7.9403	0.1010	0.0777	0.0735	4.984	2.574	2.308	3.377
Ashcroft	Taylor	$r_c = 1.9804$	−0.4628	7.9403	0.1064	0.0827	0.0775	5.362	2.656	1.968	3.558
Heine-Abarenkov	Lindhard	$r_c = 2.3724$ $u = -0.681$	−0.4693	7.9403	0.0792	0.0672	0.0549	4.745	2.348	2.346	3.147
Heine-Abarenkov	Vashishta-Singwi	$r_c = 2.354$ $u = -0.675$	−0.4718	7.9403	0.0810	0.0682	0.0573	4.833	2.383	2.394	3.200
Heine-Abarenkov	Taylor	$r_c = 2.3995$ $u = -0.706$	−0.4705	7.9403	0.0808	0.0682	0.0573	4.879	2.409	2.426	3.232
Experiments			(−0.460) (Ref. 34)	(7.9403) (Ref. 35)	(0.086) (Ref. 35)	(0.072) (Ref. 35)	(0.063) (Ref. 35)	5.17 (Ref. 38)	2.635 (Ref. 38)	2.69 (Ref. 38)	3.48 (Ref. 38) 3.69 (Ref. 37)

TABLE III. Model parameters and calculated harmonic and experimental values of static properties of K. Experimental values in the parentheses are harmonic values.

			Calculated properties								
Pseudo-potential	Dielectric function	Model parameters (a.u.)	Crystal energy (Ry/atom)	Equilibrium lattice const. (a.u.)	C_{11} (10^{12} dyne /cm^2)	C_{12} (10^{12} dyne /cm^2)	C_{44} (10^{12} dyne /cm^2)	dC_{11}/dP	dC_{12}/dP	dC_{44}/dP	$d\beta/dP$
Ashcroft	Lindhard	$r_c = 2.6190$	−0.3879	9.8624	0.0510	0.0406	0.0346	5.365	2.672	1.929	3.570
Ashcroft	Taylor	$r_c = 2.7071$	−0.3945	9.8624	0.0616	0.0491	0.0359	4.676	2.508	0.9070	3.231
Heine-Abarenkov	Lindhard	$r_c = 3.2652$ $u = -0.740$	−0.3917	9.8624	0.0384	0.0325	0.0256	4.971	2.469	2.254	3.303
Heine-Abarenkov	Vashishta-Singwi	$r_c = 3.2780$ $u = -0.738$	−0.3908	9.8624	0.0402	0.0332	0.0269	5.045	2.500	2.214	3.348
Heine-Abarenkov	Taylor	$r_c = 3.3628$ $u = -0.776$	−0.3906	9.8624	0.0407	0.0346	0.0272	5.071	2.513	2.212	3.366
Experiments			(−0.388) (Ref. 34)	(9.8624) (Ref. 35)	(0.043) (Ref. 35)	(0.035) (Ref. 35)	(0.029) (Ref. 35)	5.31 (Ref. 39)	2.808 (Ref. 39)	2.62 (Ref. 39)	3.642 (Ref. 39) 3.65 (Ref. 37)

TABLE IV. Model parameters and calculated harmonic and experimental values of the static properties of Rb. Experimental values in the parentheses are harmonic values.

			Calculated properties								
Pseudo-potential	Dielectric function	Model parameters (a.u.)	Crystal energy (Ry/atom)	Equilibrium lattice const. (a.u.)	C_{11} (10^{12} dyne /cm^2)	C_{12} (10^{12} dyne /cm^2)	C_{44} (10^{12} dyne /cm^2)	dC_{11}/dP	dC_{12}/dP	dC_{44}/dP	$d\beta/dP$
Ashcroft	Lindhard	$r_c = 2.8720$	−0.3692	10.5388	0.0431	0.0340	0.0278	4.789	2.651	1.775	3.364
Ashcroft	Taylor	$r_c = 2.959$	−0.3769	10.5388	0.0518	0.0415	0.0279	4.340	2.407	0.536	3.051
Heine-Abarenkov	Lindhard	$r_c = 4.2342$ $u = -0.977$	−0.3708	10.5388	0.0372	0.0319	0.0240	4.955	2.476	2.279	3.302
Heine-Abarenkov	Vashishta-Singwi	$r_c = 3.7210$ $u = -0.808$	−0.3697	10.5388	0.0318	0.0263	0.0207	5.064	2.516	2.174	3.365
Heine-Abarenkov	Taylor	$r_c = 3.8363$ $u = -0.849$	−0.3695	10.5388	0.0322	0.0265	0.0209	5.093	2.527	2.172	3.382
Experiments			(−0.370) (Ref. 34)	(10.5388) (Ref. 35)	(0.035) (Ref. 35)	(0.030) (Ref. 35)	(0.022) (Ref. 35)	4.96 (Ref. 40)	2.502 (Ref. 40)	2.48 (Ref. 40)	3.321 (Ref. 40) 3.37 (Ref. 37)

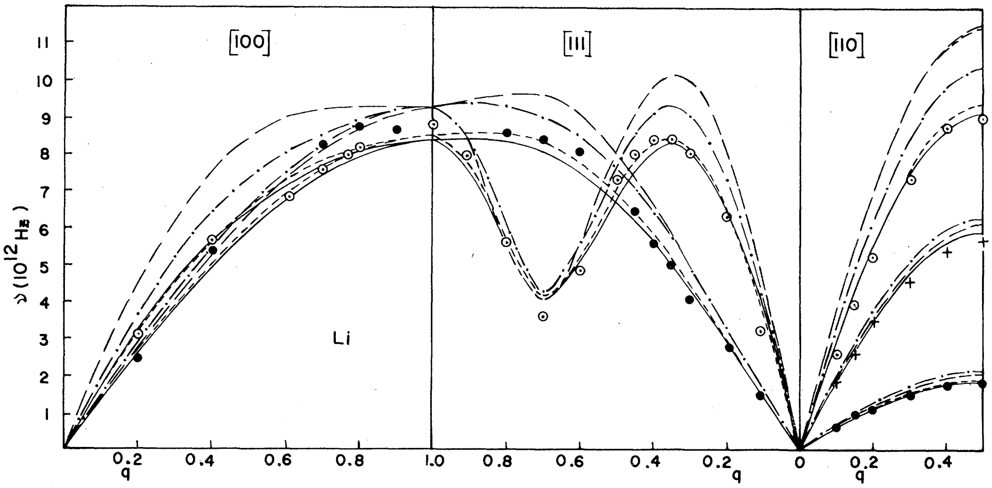

FIG. 2. Phonon dispersion curves for Li at 90 K for different potential dielectric function combinations. (a) — — — Ashcroft + Lindhard, (b) —·—·—·— Ashcroft + Taylor, (c) — — — — — Heine-Abarenkov + Lind, (d) - - - - - Heine-Abarenkov + Vashista-Singwi, (e) ——— Heine-Abarenkov + Taylor. Experimental points which are taken from Smith *et al.* (Ref. 41) are indicated by ○ for longitudinal branches and ● and × for transverse branches.

while tackling this problem in the framework of a phenomenological model, came to the conclusion that the inclusion of at least three-body terms in the dynamical matrix is an absolute necessity for the reproduction of this crossover.

Results of the calculation of phonon frequencies with different models together with the experimental values have been shown in Figs. 2–5.

Mode Grüneisen parameters for Na and K have been calculated using Vashishta-Singwi as well as Taylor dielectric functions combined with the Heine-Abarenkov potential. The two dielectric functions again give similar results. For Na, a few experimental data[25] are available at low q values. For these q values, our calculated results agree very well with the experiment and are always within experimental errors. For K, the agreement with the experiment[26] is not so good. Taylor *et al.*[27] have pointed out that this discrepancy is common to all pseudopotential calculations. In the present case, the agreement is not worse than any of the calculations existing in the literature.[27–33] The calculated and experimental results are shown in Figs. 6 and 7.

For the entire set of static and dynamic properties of metals under study, roles played by analytical $\epsilon_{\mathrm{VS}}(q)$ and $\epsilon_T(q)$ seem to be identical. This may appear surprising as their "effective-interaction" curves are widely different. On comparing, however, the correction-factor curves for $\epsilon_{\mathrm{VS}}(q)$ (an-

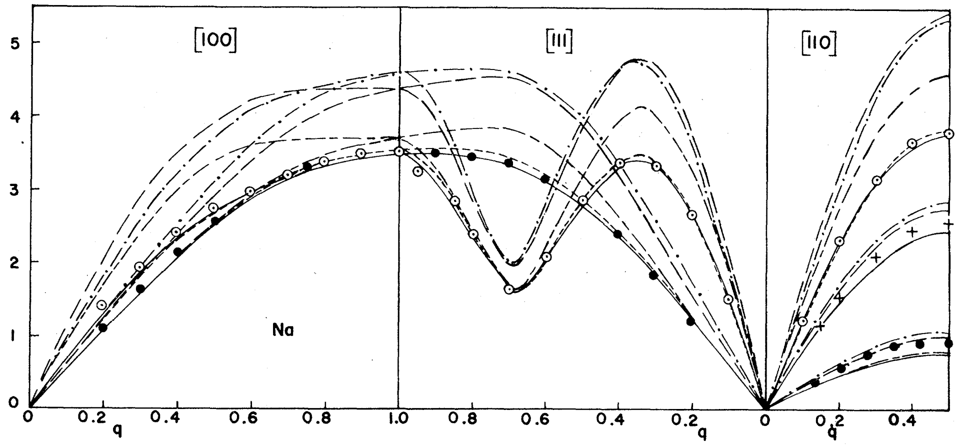

FIG. 3. Phonon-dispersion curves for Na along symmetry directions at 90 K. Experimental points are taken from Woods *et al.* (Ref. 42). Other descriptions are the same as in Fig. 1.

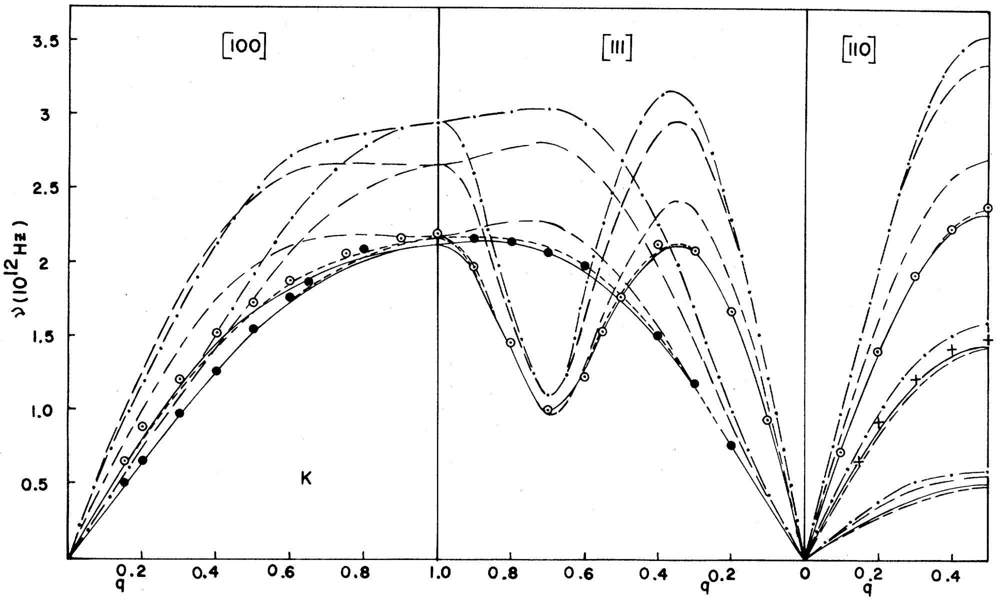

FIG. 4. Phonon dispersion curves for K at 9 K. Experimental points are taken from Cowley *et al.* (Ref. 43). Other descriptions are the same as in Fig. 1.

alytical) and $\epsilon_T(q)$, we find them to be very close in the region $q \geq 0.8k_F$. For $q < 0.8k_F$, there is a significant difference but there is no reflection of this difference in the corresponding calculated values of different properties. We conclude, therefore, that the correction factor to $\epsilon(q)$ is important in the region $0.8k_F \leq q \leq 2k_F$. Beyond $2k_F$ the correction factor is insignificant. Probably, the region $q \leq 0.8k_F$ would be important if one used the long-wave theory for the calculation of elastic constants, in which case, we believe, ϵ_{VS} (analytical) would give results considerably different from ϵ_T, as is evident from the curves in Fig. 1.

The discrepancies still remaining may be due to one or more of the following causes.

(i) In the present calculation we have neglected the third- and fourth-order-perturbation terms. It has been shown by Brovman *et al.*[1] that these terms have contributions which are not always negligible.

(ii) We have restricted ourselves to harmonic approximations. But anharmonic effects may be playing a significant role in some cases.

(iii) We have calculated harmonic values of static properties. But the want of sufficient experimental data (particularly in the case of pressure derivatives of elastic moduli) for the extrapolation to harmonic values, may lead to significant error in

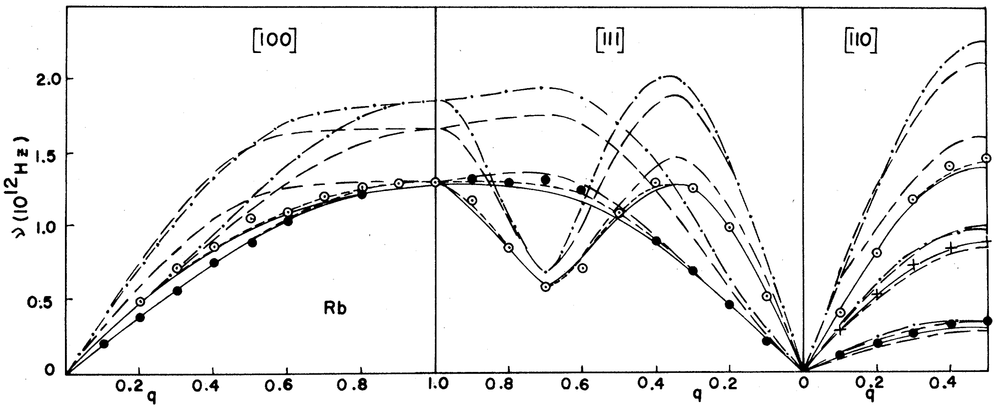

FIG. 5. Phonon dispersion curves for Rb at 120 K. Experimental points are taken from Copley *et al.* (Ref. 44). Other descriptions are the same as in Fig. 1.

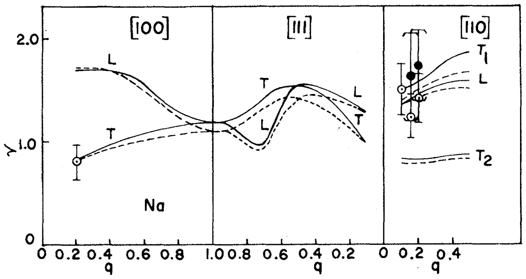

FIG. 6. Calculated mode Grüneisen parameters for Na corresponding to H-A + Vashishta-Singwi (broken curve) and H-A + Taylor (full curve) combinations. Experimental points which are taken from Ernst *et al.* (Ref. 25) are indicated by ○ for longitudinal, ● for transverse (T or T_1), and ⊗ for transverse (T_2) branches.

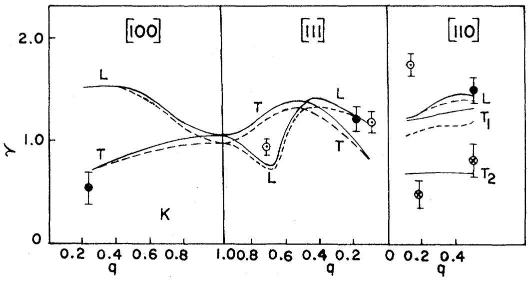

FIG. 7. Mode Grüneisen parameters for K. Experimental results are taken from Meyer *et al.* (Ref. 26). Other descriptions are the same as in Fig. 6. For the [110] T_2 mode both curves coincide.

our estimate of the harmonic data.

(iv) The local nature of the pseudopotential used in our analysis may also introduce some discrepancies. Particularly for Li, nonlocality seems to be important.

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