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Phonon spectra of alkali metals in real space

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The exponentially damped two-body interaction obtained in second-order perturbation theory using the rational dielectric function and the Heine-Abarenkov model potential is used to calculate the phonon spectra of alkali metals. The interaction is also used to predict the binding energy and elastic constants of these solids. The calculations are repeated using the Lindhard-Taylor dielectric function and compared. The calculations of phonon spectra using the Lindhard-Taylor dielectric function are performed in wave-number space, as usual. The results obtained using the two screening functions are exactly the same as were expected. It is found that the use of an exponentially damped pair potential for obtaining phonon spectra of a metal at the same number of points reduces the computer time by about 90%.

I. INTRODUCTION

The Hartree dielectric function for screening due to electrons with or without modifications combined with a pseudopotential is used to write down the ion-ion interaction in second-order perturbation theory.[1] Using this interaction Soma *et al.*[2] obtained the elastic constants of alkali metals very recently. The structure in the effective interaction is intimately associated with the logarithmic singularity at $q=2k_F$ in wave-number space. The long-range Friedel oscillations are, in turn, responsible for poor convergence of the force constants between ions obtained with two-body interaction, therefore, the calculations of phonon spectra are being performed in reciprocal space.[1,3] The calculations in wave-number space have indicated that this singularity has very limited impact on the properties of interest; while it does give Kohn anomalies in vibrational spectrum. The general form of the spectrum does not depend upon the singularity. This explains why the effective interaction between ions can be so sensitive and uncertain, while the mathematically equivalent calculations in wave-number space can be quite stable but insensitive. This suggests that we may simplify the screening to obtain a suitable and simple interionic interaction which still could give a good account of most properties of the metals.[4]

The replacement of the Hartree dielectric function with its logarithmic singularity by the rational dielectric function[5] is a good choice. The rational function reproduces the Hartree function exactly except its logarithmic singularity. It has the correct low- and high-q behavior and is 0.5 at $q=2K_F$. The rational dielectric function combined with a pseudopotential gives rise to a simple analytic form of the ion-ion pair potential[6] in second-order perturbation theory. The exponentially damped pair potential has the advantage of not containing the very long-range Friedel oscillations. It is found that the sum of first three damped oscillatory contributions to the pair potential is sufficient to explain the structural phase transitions of Na, Mg, and Al under pressure.[6] In the present work, we calculate the binding energy, the elastic constants, and phonon spectra of alkali metals using the exponentially damped pair potential, which leads to rapidly converging calculations. It is found that even properties such as elastic constants and phonon spectra can be treated entirely in terms of a simple and fast converging two-body interaction.

II. THE EFFECTIVE INTERACTION BETWEEN IONS AND DYNAMICAL MATRIX

For a system of N ions of valence Z and which are held in a finite volume V, the total energy within the local pseudopotential model taken to second-order may be written as[7]

$$-E_{\mathrm{BI}}=E_{\mathrm{eg}}(n_0)+\tfrac{1}{2}V_{\mathrm{bs}}(r=0)+\tfrac{1}{2}\sum_{i\neq 0}V(\mathbf{r}_i)\ . \tag{1}$$

$E_{\mathrm{eg}}(n_0)$ is the energy of all electrons in a homogeneous electron gas of density $n_0=NZ/V$. The exchange-correlation corrections appropriate to the metallic densities[8] have been included in $E_{\mathrm{eg}}(n_0)$. V_{bs} $(r=0)$ is obtained from the band-structure part of the energy by evaluating the integral appearing in it in conjunction with the rational dielectric function and the Heine-Abarenkov[3] model potential.

The derivation of ion-ion interaction in second-order perturbation theory using rational dielectric function in conjunction with pseudopotential is carried out by Ward[9] in detail. Here, we simply note that the part of the effective potential exactly cancels the electrostatic Coulomb repulsion and within linear screening theory the remainder is an effective screened Coulomb potential, given for Heine-Abarenkov[3] pseudopotential by

$$V(r)=\frac{Z^2e^2}{r}\sum_{n=1}^{3}A_n\cos(k_nr+\alpha_n)\exp(-\lambda_nr)\ , \tag{2}$$

where the amplitude A_n is given by

$$A_n = 2d_n |\hat{v}(q_n)|^2 , \tag{3}$$

and the phase α_n is given by

$$\alpha_n = \delta_n + 2\arg\hat{v}(q_n) . \tag{4}$$

The modulus of the normalized Heine-Abarenkov model potential $\hat{v}(q_n) = D \sin q_n r_c / q_n r_c + (1-D)\cos q_n r_c$, where D and r_c are potential parameters, is defined as

$$|\hat{v}(q_n)| = \left[\frac{D^2}{2(k_n^2+\lambda_n^2)r_c^2}(\cosh 2\lambda_n r_c - \cos 2k_n r_c) + \frac{(1-D)^2}{2}(\cosh 2\lambda_n r_c + \cos 2k_n r_c) + \frac{D(1-D)}{(k_n^2+\lambda_n^2)r_c}(\lambda_n \sinh 2\lambda_n r_c + k_n \sin 2k_n r_c) \right]^{1/2} , \tag{5}$$

and

$$\arg\hat{v}(q_n) = \tan^{-1} \left[\frac{\frac{D}{(k_n^2+\lambda_n^2)r_c}(k_n \tanh\lambda_n r_c - \lambda_n \tan k_n r_c) - (1-D)\tanh\lambda_n r_c \tan k_n r_c}{\frac{D}{(k_n^2+\lambda_n^2)r_c}(\lambda_n \tanh\lambda_n r_c + k_n \tan k_n r_c) + (1-D)} \right] . \tag{6}$$

The parameters k_n, λ_n, d_n, and δ_n are functions of the electron radius[6] r_s. $q_n = k_n + \iota\lambda_n$ is the pole of the inverse dielectric function.

Using the interionic potential $V(r)$, we obtain the radial K_r and tangential K_t force constants given by

$$K_r = \frac{d^2V(r)}{dr^2} ,= \frac{Z^2e^2}{r^3} \sum_{n=1}^{3} A_n \cos(k_n r + \alpha_n)\exp(-\lambda_n r)[2 + 2\lambda_n r + \lambda_n^2 r^2 - k_n^2 r^2 + 2k_n r(1+\lambda_n r)\tan(k_n r + \alpha_n)] , \tag{7}$$

and

$$K_t = \frac{1}{r}\frac{dV(r)}{dr} = -\frac{Z^2e^2}{r^3} \sum_{n=1}^{3} A_n \cos(k_n r + \alpha_n)\exp(-\lambda_n r)[1 + \lambda_n r + k_n r \tan(k_n r + \alpha_n)] . \tag{8}$$

In the limits $k_n \to 0$ and $\delta_n \to 0$, Eq. (2) reduces to the analytic expression for effective potential

$$V_{\mathrm{TF}}(r) = \frac{Z^2e^2}{r} \left[D\frac{\sinh\lambda r_c}{\lambda r_c} + (1-D)\cosh\lambda r_c \right]^2 \times \exp(-\lambda r) , \tag{9}$$

in the Thomas-Fermi approximation, provided one sets λ_n equal to the Thomas-Fermi inverse screening length λ and $2\sum_{n=1}^{3} d_n = 1$. Similarly, the expression of radial and tangential force constants given by Eqs. (7) and (8) reduce to

$$K_r = V_{\mathrm{TF}}(r)\frac{2 + 2\lambda r + r + \lambda^2 r^2}{r^2} , \tag{10}$$

and

$$K_t = -V_{\mathrm{TF}}(r)\frac{1+\lambda r}{r^2} , \tag{11}$$

respectively, in the Thomas-Fermi approximation. For the empty-core pseudopotential Eq. (9) reduces to the expression

$$V_{\mathrm{TF}}(r) = \frac{Z^2e^2}{r}\cosh^2\lambda r_c \exp(-\lambda r) . \tag{12}$$

The effective potential defined by Eq. (12) is also obtained by Harrison and Wills.[4]

From K_r and K_t at any interionic separation, we obtain the interionic force constant $K_{\alpha\beta}$ defined as the tensor given by

$$K_{\alpha\beta} = \frac{d^2V(r)}{dr_\alpha dr_\beta} = \left[\delta_{\alpha\beta} - \frac{r_\alpha r_\beta}{r^2} \right] K_t + \frac{r_\alpha r_\beta}{r^2} K_{r'} . \tag{13}$$

From the interionic force constants $K_{\alpha\beta}$ at nth neighbor separation, we obtain the elastic constants for alkali metals by using the dynamical long-wave phonon method.[10] Finally

$$D_{\alpha\beta}(\mathbf{q}) = \sum_l K_{\alpha\beta}(\mathbf{r}_l)[1 - \exp(-i\mathbf{q}\cdot\mathbf{r}_l)] , \tag{14}$$

was used to generate the phonon frequencies.

TABLE I. Binding energy $-E_{\mathrm{BI}}$ (eV/atom) obtained using Eq. (1). *a*, the Pettifor[5] dielectric function; *b*, the Lindhard-Taylor[13] dielectric function.

	Li	Na	K	Rb	Cs
a	7.340	6.139	5.205	4.980	4.688
b	7.469	6.318	5.303	5.022	4.696
Expt.[a]	7.020	6.253	5.274	5.032	4.694

[a]Experimental values are estimated using the relation, $-E_{\mathrm{BI}}=-E_{\mathrm{coh}}-E_I$, from the data summarized by Kittel (Ref. 20). Here E_{coh} and E_I are cohesive energy and first ionization energy, respectively.

III. NUMERICAL RESULTS

In numerical calculations we use observed[11] atomic radii for all alkali metals. The potential parameters are taken the same as has been reported by Popovic *et al.*[12] Theoretical results of binding energy and elastic constants have been found in good agreement with their experimental values and are compared in Tables I and II, respectively. Meaningful but not very accurate results can be obtained in some cases including only a few nearest neighbors, here we carry each calculation to convergence. On the other hand, one has to include contribution beyond the tenth shell to get meaningful results using two-body interaction defined with Lindhard-Taylor[13] dielectric function, here we have included contribution up to 16th shell. The values of binding energy and elastic moduli obtained using the Lindhard-Taylor[13] dielectric function are also given in Tables I and II, respectively, for comparison. The elastic moduli obtained using the two screening functions are almost the same as were expected.

The phonon frequencies of alkali metals along three symmetry directions are shown in Figs. 1–5 as obtained with Eqs. (2)–(8) and (14) along with experimental results. The values obtained in wave-number space[1] using the Lindhard-Taylor[13] dielectric function are shown by dashed lines in the respective figure of each metal. As expected, the two results obtained using the two screening functions agree very well. It is found that the exponentially damped pair potential reproduces the experimental results reasonably well for all alkali metals in the long-wavelength region. As a result, the calculated elastic moduli were in good agreement with experimental values. Comparing the phonon frequencies near zone boundary, it is found that the agreement with experimental values improves dramatically as we move towards heavier elemental metals. In case of Rb and Cs, some discrepancies of calculated results with experiments are bound to occur as some important contributions arising because large core size and *s*-*d* mixing have been neglected in the present second-order perturbation treatment. For example, the comparison of the density-of-states effective mass m^* for Rb on the Fermi surface in the [100], [110], and [111] directions, calculated[14] by solving the secular determinant being 0.99, 1.05, and 0.94, respectively, compared with the value 1.17 from first-order perturbation theory, indicates that we might have different errors by neglecting third- and higher-order contributions. Similarly for Cs, comparison of m^* (0.98, 1.17, and 0.90 versus 0.84) indicates that higher-order perturbation corrections might be important. The contribution due to *s*-*d* hybridization, though its effect on $\omega(\mathbf{q})$ even for Cs is negligible,[15] may also add to some discrepancy. An important contribution arising due to orthogonalization-hole[16] correction, which has been neglected here, may also cause some error. Therefore, such an agreement of calculated results with experiments for Rb and Cs should not be considered seriously, especially, when so many important contributions have been left out in the treatment of lattice dynamical properties and elastic constants.

Here we should note that we have avoided the model potential parameter fitting since our aim is to learn about the validity of this approach. The calculations up to the seventh shell have been found sufficient to achieve convergence for these calculations. However, to achieve convergence of the same order in performing the calculation of phonon spectra in reciprocal space with usual practice, i.e., using the effective potential defined with the Lindhard-Taylor[13] dielectric function in second-order perturbation theory, one has to include contribution up to the twenty-seventh shell. Thus a numerical calculation of phonon spectra in all seven branches of three symmetry directions using the present pair potential requires about one-tenth of computer time than that required by the calculation of it in wave-number space at same number of points using the Lindhard dielectric function. It is to be noted that in the present method, there is no need to calculate the electrostatic Coulomb part of the phonon frequencies, as a part of the band structure exactly cancels the electrostatic Coulomb repulsion in the effective potential.

TABLE II. The calculated elastic constants of alkali metals. The experimental data is summarized by Shimada (Ref. 21) and Huntington (Ref. 22). *a*, the Pettifor dielectric function; *b*, the Lindhard-Taylor dielectric function.

	C_{11} (Mbar)			C_{12} (Mbar)			C_{44} (Mbar)		
	a	*b*	Expt.	*a*	*b*	Expt.	*a*	*b*	Expt.
Li	0.168	0.168	0.157	0.144	0.143	0.133	0.111	0.110	0.116
Na	0.110	0.098	0.095	0.091	0.086	0.078	0.063	0.059	0.062
K	0.045	0.041	0.042	0.037	0.035	0.034	0.027	0.026	0.029
Rb	0.033	0.031	0.032	0.027	0.026	0.026	0.020	0.020	0.021
Cs	0.023	0.022	0.026	0.019	0.019	0.022	0.015	0.014	0.016

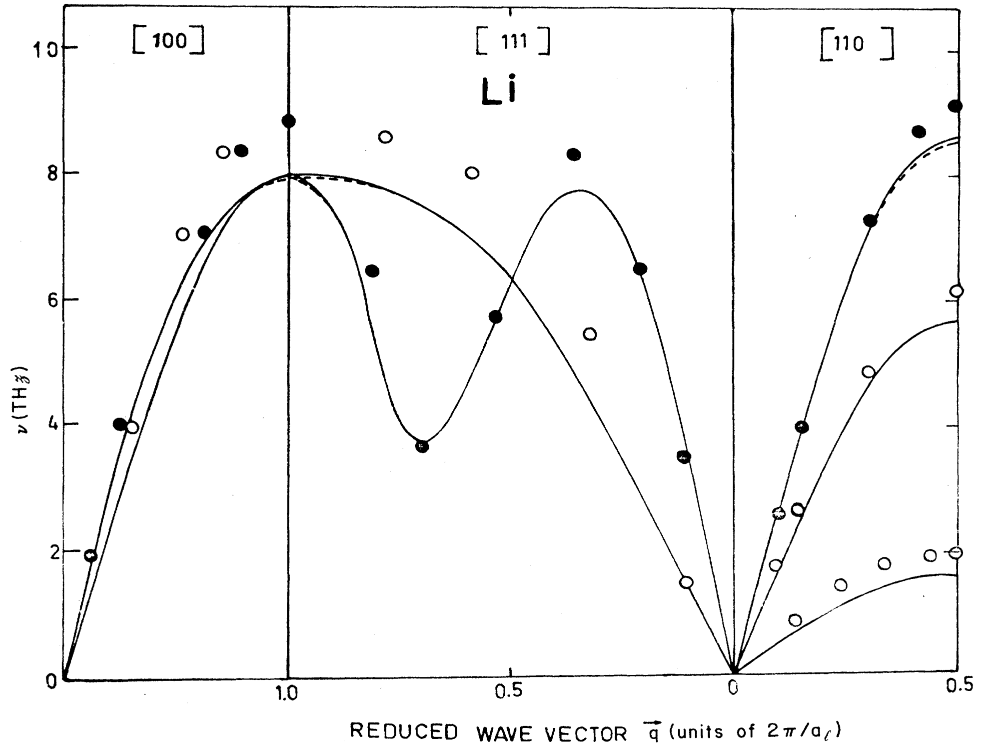

FIG. 1. Dispersion curves of Li along symmetry directions. The solid and dashed curves represent the present calculations in real and wave-number space, respectively. The points are the experimental data by Smith *et al.* (Ref. 23) at 98 K. a_l is the lattice parameter.

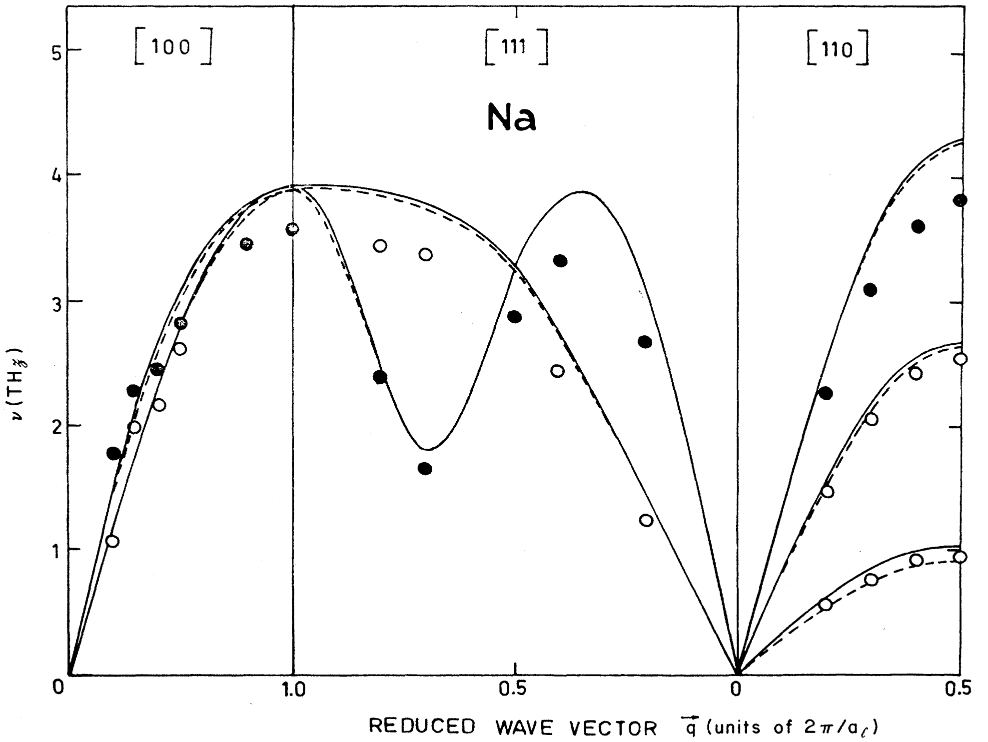

FIG. 2. Dispersion curves of Na. The points are experimental data by Woods *et al.* (Ref. 24) at 90 K. The rest of the description is the same as that of Fig. 1.

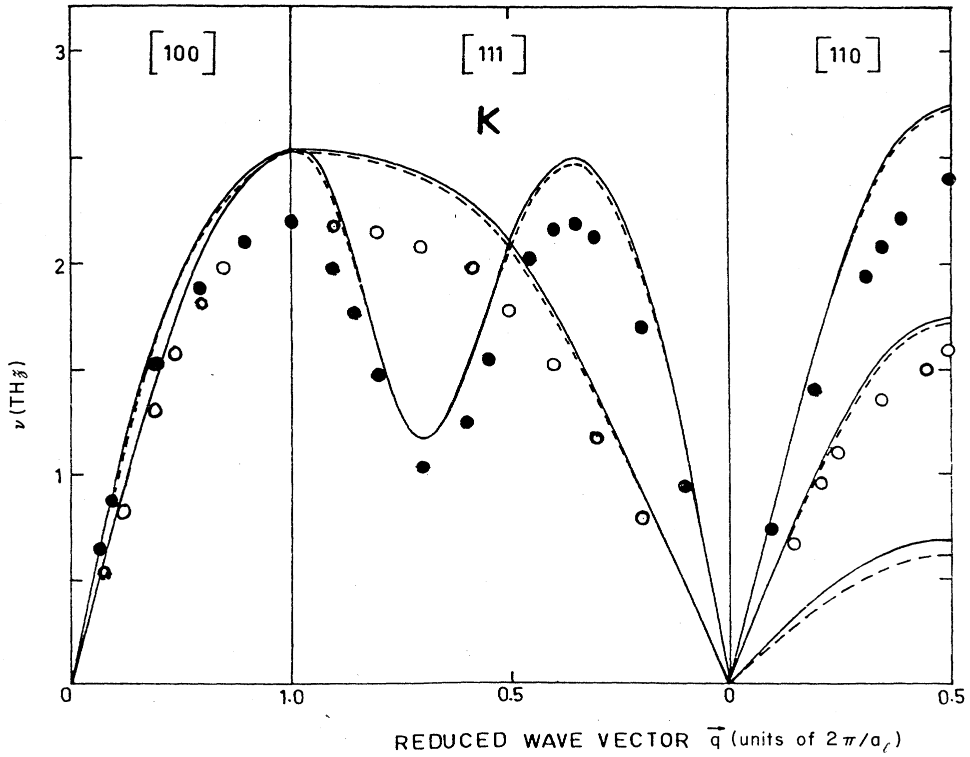

FIG. 3. Dispersion curves of K. The points are experimental data by Cowley *et al.* (Ref. 25) at 9 K. The rest of the description is the same as that of Fig. 1.

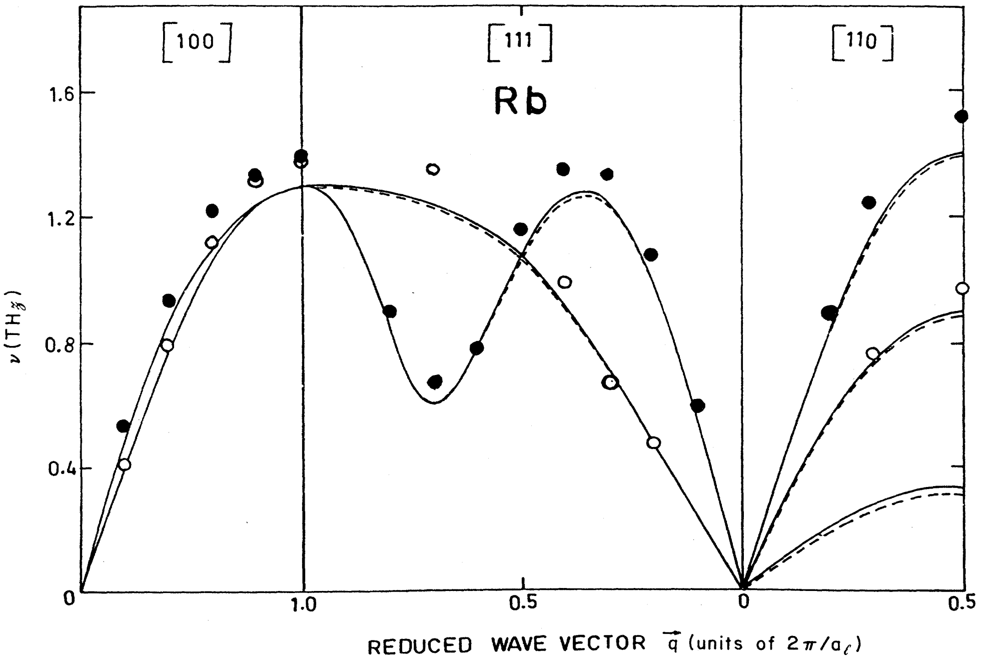

FIG. 4. Dispersion curves of Rb. The points are experimental data by Copley *et al.* (Ref. 26) at 12 K. The rest of the description is the same as that of Fig. 1.

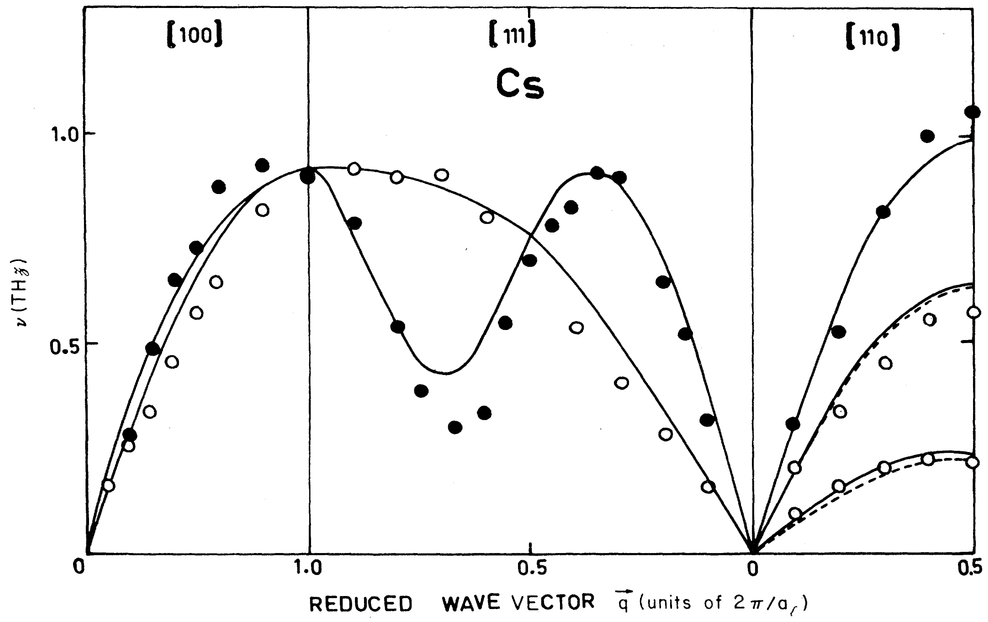

FIG. 5. Dispersion curves of Cs. The points are experimental data by Mitzuki and Stassis (Ref. 27) at 280 K. The rest of the description is the same as that of Fig. 1.

IV. CONCLUSIONS

In summary use of the rational dielectric function has eliminated the complexity and slow convergence of two-body interaction obtained using the Hartree dielectric function. Its prime virtue is its simplicity and ease of application. This approach can easily be extended to calculate the elastic properties of the entire range of simple metals and their alloys. Several first-principle theories[17–19] have been used in the past to study phonon spectra, elastic constants, and other properties of alkali metals both in crystalline and liquid phase. Use of this two-body potential makes the assessment of these properties comparatively easy. The use of this pair potential for calculating the elastic and dynamical properties of a metal reduces the computer time manifold. It is to be noted that the exchange-correlation corrections due to Taylor[13] are inherited in the rational dielectric function through its parameters.

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