

Lattice Dynamics of hcp Metals Computed from an Optimum-Model Potential

G. GILAT* AND G. RIZZI

Comitato Nazionale per l'Energia Nucleare, Ispra (Varese), Italy

AND

G. CUBIOTTI

Istituto di Fisica, Università di Messina, Messina, Italy

(Received 11 December 1968)

In recent papers by Shaw and Harrison and by Shaw, the model potential due to Heine, Abarenkov, and Animalu has been reformulated and optimized. This optimum-model potential is employed to obtain energy-wave-number characteristics, from which the phonon dispersion relations for beryllium, magnesium, and zinc are computed. The results of these calculations are compared with experimental results for high-symmetry directions. The fit is unsatisfactory for Be, somewhat better for Mg, and fairly good for Zn. The non-local part of the optimum-model potential does not play a significant role for Be and Mg, but is quite important in the case of Zn. By using values higher than unity for m^* (the effective mass of the electron, in a.u.), the fit to experimental results could be substantially improved in the case of Mg. On employing m^* as an adjustable parameter, a remarkably good fit to the experimental data for Mg was achieved with $m^* = 1.60$.

I. INTRODUCTION

IN recent years, there has been an increasing interest in the pseudopotential approach in the theory of simple metals, and in its application to computations of phonon dispersion relations. Pioneer calculations in lattice dynamics were carried out by Harrison¹ and Toya.² Following these early attempts, Cochran³ performed a semiempirical type of calculation, where he used the measured phonon data of Na to obtain the empirical pseudopotential for that metal. Another relatively early calculation was performed by Sham.⁴ Since then, there have been many more publications relevant to this subject, and it would be, perhaps, the task of a review article to attempt an exhaustive summary of contributions in this field. A significant general observation, however, is that the success of this approach in predicting experimental values for phonon-dispersion relations is remarkably good for the alkali metals Na and K, and less so in increasing order for metals such as Al and Pb. The valence of the metal seems to be a major factor in the degree of such success.⁵ It is interesting to point out that also in the case of Li the agreement between experiment and theory has been quite poor.⁶

Most of the calculations in the past have been applied to monatomic cubic crystals. This fact is of no particular relevance to the pseudopotential approach as such, and the reason for this is perhaps that for this structure nu-

merical calculations are simpler. In the present case, however, we confine ourselves to hexagonal metals, and it would be worthwhile to give a somewhat more detailed account of earlier similar calculations of these metals. The first such computation was carried out by Roy and Venkataraman,⁷ who applied the pseudopotential approach to Mg, which is a hcp metal. RV unfortunately included two errors in their published article, and therefore we do not refer to their fit to the experimental data as given in this paper.⁷ In a subsequent addendum,⁸ however, RV corrected these errors and presented a new fit of their calculations to experiment.⁹ The agreement between theory and experiment in this addendum is fair, the calculated longitudinal modes being some 20% too low in frequency, and the transverse modes some 10% too high. The inclusion of two disposable parameters significantly improved the fit for the longitudinal modes, but worsened it for the transverse phonons.

In another paper by Brovman, Kagan, and Holas,¹⁰ the pseudopotential approach was used for the calculation of phonon-dispersion relations in Mg, Be and Zn. Comparison between theory and experiment in the case of Mg shows that the computed longitudinal and transverse frequencies are some 30 and 10% too high, respectively. In the case of Be, the agreement between theory and experiment¹¹ is even worse for the longitudinal modes, the calculated frequencies being higher by almost a factor of 2. In the case of Zn, the theoretical results are

* On temporary leave from Department of Physics, Technion-Israel Institute of Technology, Haifa, Israel.

¹ W. A. Harrison, Ph.D. thesis, University of Illinois, 1956 (unpublished).

² T. Toya, *J. Res. Inst. Catalysis Hokkaido Univ.* **6**, 161 (1958); **6**, 183 (1958); **7**, 60 (1959).

³ W. Cochran, *Proc. Roy. Soc. (London)* **A276**, 308 (1963).

⁴ L. J. Sham, *Proc. Roy. Soc. (London)* **A283**, 33 (1965).

⁵ W. A. Harrison (private communication).

⁶ G. Dolling (private communication). The experimental data were taken by H. G. Smith, G. Dolling, R. M. Nicklow, P. R. Vijayaraghavan, and M. K. Wilkinson, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1968), Vol. I, p. 149.

⁷ A. P. Roy and G. Venkataraman, *Phys. Rev.* **156**, 769 (1967), hereafter referred to as RV.

⁸ A. P. Roy and G. Venkataraman, addendum to Ref. 8 (unpublished).

⁹ P. K. Iyengar, G. Venkataraman, P. R. Vijayaraghavan, and A. P. Roy, in *Inelastic Scattering on Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 153.

¹⁰ E. G. Brovman, Yu. Kagan, and A. Holas, *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1968, hereafter referred to as BKH), Vol. I, p. 165.

¹¹ R. E. Schmunk, R. M. Brugger, P. D. Randolph, and K. A. Strong, *Phys. Rev.* **128**, 562 (1962).

very poor, for two of the branches yield imaginary frequencies for most of the range in the directions of $\Delta(0,0,0,1)$, $\Sigma(0,1,1,0)$, and T and T' $(1,1,2,0)$. The rest of the modes bear more resemblance to reality, though they are about 30% too low when compared with experimental data.¹² BKH improved, very significantly, the agreement between experiment and theory for all three metals by allowing for four disposable parameters for each metal. BKH claim that in the case of these metals, as well as in the case of β -Sn,¹³ one must include many-body forces which arise from multiple scattering of conduction electrons by ions. These forces are most significant for short-range interactions and should, therefore, show up as sizable contributions to nearest-neighbor interactions in the framework of the Born-von Kármán theory.

During the course of time, there have also been some significant new developments in the theory of pseudopotentials itself. In a series of articles¹⁴⁻¹⁷ by Heine, Abarenkov, and Animalu (HAA), a new approach based on the quantum defect method¹⁸ was formulated. In this approach, the metallic ion is considered to be a sphere of radius R_M , and the effective potential, or the model potential as termed by HAA, is given by

$$\begin{aligned} V(r) &= -\sum_l A_l(E) P_l \quad (r < R_M) \\ &= -Ze/r \quad (r \geq R_M), \end{aligned} \quad (1.1)$$

where $A_l(E)$ are parameters depending on the angular momentum l and on the energy E of the conduction electrons which interact with this potential. The P_l are projection operators which sort out from the total wave function of the electron the partial wave characterized by angular momentum quantum number l . The parameters A_l reflect the atomic structure of the ions embedded in the metal. For ions with empty f shells $l \leq 2$, and this is the range of angular momenta to which HAA apply their model. R_M is chosen in a somewhat arbitrary way, so that it is as close as possible to Z/A_0 . The logarithmic derivative of the wave functions as well as the potential $V(r)$ experiences a discontinuity at $r=R_M$. For a better description of the model potential, the reader is referred to the original papers¹⁴⁻¹⁷ or to Harrison.¹⁹ One consequence of the model potential which is of importance in this context is that when Fourier-transformed into momentum space, it yields local as well as nonlocal contributions. This complicates,

¹² G. Borgonovi, G. Caglioti, and J. J. Antal, Phys. Rev. **132**, 638 (1963).

¹³ E. G. Brovman and Yu. Kagan, Zh. Esperim. i Teor. Phys. **52**, 557 (1966) [English transl.: Soviet Phys.—JETP **25**, 365 (1966)].

¹⁴ V. Heine and I. V. Abarenkov, Phil. Mag. **9**, 451 (1964).

¹⁵ A. O. E. Animalu, Phil. Mag. **11**, 379 (1965).

¹⁶ I. V. Abarenkov and V. Heine, Phil. Mag. **12**, 529 (1965).

¹⁷ A. O. E. Animalu and V. Heine, Phil. Mag. **12**, 1249 (1965).

¹⁸ F. S. Ham, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 127.

¹⁹ W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

to some extent, the computations in comparison with the simpler local pseudopotentials used previously.

In a more recent paper by Shaw and Harrison,²⁰ the HAA model potential has been reformulated so that a minor arbitrariness in the original HAA model could be avoided. They also chose R_M in such a way that the logarithmic derivative of the wave function is continuous at R_M . In their paper, Shaw and Harrison also calculate the charge-density distribution of the conduction electrons over the ionic core volume and show that one must correct for the ion valence Z . In a still more recent paper by Shaw,²¹ a few additional modifications of the model potential are considered. These are described in Sec. II.

Throughout the present work we use the formalism developed by Harrison.¹⁹ We also try to use Harrison's notation as far as possible. In Sec. II, we give a description of the theoretical background needed for the calculation of the pseudopotential. In Sec. III, we present the results of the computations of the pseudopotential. In Sec. IV, we describe the calculation of the phonon dynamical matrix as based on the pseudopotential approach. The computational results of phonon dispersion relations for Be, Mg, and Zn are given in Sec. V, and in Sec. VI, we summarize the paper.

II. OPTIMUM MODEL POTENTIAL

Our present computations are based on a so-called optimum model potential recently proposed by Shaw.²¹ This potential is an optimized variant of the HAA model potential¹⁴⁻¹⁷ and differs from it in a few respects.

(a) The ionic core radius in the HAA model is given by a single parameter R_M , whereas Shaw allows for different R_l , depending on the angular momentum l .

(b) The model parameters $A_l(E)$ in the HAA model are computed at $E=E_F$, where E_F is the conduction-electron Fermi energy. Shaw, in contrast, takes into account also the energy dependence of $A_l(E)$ in its first (linear) approximation, i.e.,

$$A_l(E) = A_l(E_F) + \frac{1}{2}(k^2 - k_F^2)(\partial A_l / \partial E)_{E_F}, \quad (2.1)$$

where k_F is the Fermi wave-number, and the relation is given in atomic units.²²

(c) The optimum model potential used by Shaw²¹ is given by

$$w_0(r) = -\frac{Z}{r} - \sum_l \Theta(R_l - r) \left(A_l - \frac{Z}{r} \right) P_l, \quad (2.2)$$

where $\Theta(R_l - r)$ is a step function defined by

$$\begin{aligned} \Theta(R_l - r) &= 1 \quad (r < R_l) \\ &= 0 \quad (r \geq R_l), \end{aligned} \quad (2.3)$$

²⁰ R. W. Shaw, Jr., and W. A. Harrison, Phys. Rev. **163**, 604 (1967).

²¹ R. W. Shaw, Jr., Phys. Rev. **174**, 769 (1968). We are indebted to Dr. Shaw for sending us a report of the above and some extra calculations prior to publication.

²² Throughout this paper we use atomic units, unless it is otherwise specified. The a.u. of energy is 2 Ry.

and P_1 are projection operators given by

$$P_l = \sum_{m=-l}^l |Y_l^m\rangle\langle Y_l^m|. \quad (2.4)$$

In comparison with (2.2), HAA use as the model potential for $r < R_M$ the expression

$$w_0 = -(A_0 - A_2)P_2 - (A_1 - A_2)P_1 - A_2. \quad (2.5)$$

(d) Shaw optimizes his model potential by choosing for R_l

$$R_l(E) = Z/A_l(E). \quad (2.6)$$

This choice is consistent with the smooth behavior of the wave function at $r = R_l$, but it also provides for continuity in $w_0(r)$ at this point. This choice avoids the long-range oscillations in momentum space which are characteristic of the HAA model potential.

Once given a certain effective (model) potential in r space, one can apply the formalism described by Harrison¹⁹ in order to obtain the unscreened form factor $w_0(\mathbf{k}, \mathbf{q})$, which, in the present case, consists of local as well as nonlocal contributions²¹:

$$w_0(\mathbf{k}, \mathbf{q}) = v(\mathbf{q}) + v_d(\mathbf{q}) + f(\mathbf{k}, \mathbf{q}), \quad (2.7)$$

where k is the conduction-electron wave-number vector specifying the electron state, and \mathbf{q} is the wave vector involved in the scattering of an electron. By the nonlocal and local contributions we mean, respectively, the \mathbf{k} -dependent and \mathbf{k} -independent terms that enter into (2.7). The terms themselves are

$$v(\mathbf{q}) + v_d(\mathbf{q}) = -4\pi Z^*/\Omega_0 q^2, \quad (2.8)$$

which is the Coulomb part of the potential. Ω_0 is the atomic volume, and Z^* is the effective valence of the ion already including the "depletion-hole"²⁰ charge density ρ .

$$Z^* = Z(1 - \rho/Z). \quad (2.9)$$

The nonlocal part of the unscreened form factor is given by

$$f(\mathbf{k}, \mathbf{q}) = -\frac{4\pi Z}{\Omega_0} \sum_l (2l+1) P_l(\cos\theta) R_l^2(E) \times \int_0^1 dx x(x-1) j_l(k'R_l x) j_l(kR_l x), \quad (2.10)$$

where $j_l(y)$ is the spherical Bessel function of order l . The angular momentum quantum number l can have the values $l=0, 1, 2$ for all metals with an empty 3f shell. $P_l(\cos\theta)$ is the Legendre polynomial of order l , and θ is the angle between \mathbf{k} and $\mathbf{k}' = \mathbf{k} + \mathbf{q}$. Our next step, following Harrison,¹⁹ is to screen $w_0(\mathbf{k}, \mathbf{q})$. This is accomplished by finding the screening field $w_1(q)$ and adding it to $w_0(\mathbf{k}, \mathbf{q})$. The resultant screened form factor $w(\mathbf{k}, \mathbf{q})$ is now defined by

$$w(\mathbf{k}, \mathbf{q}) = w_0(\mathbf{k}, \mathbf{q}) + w_1(q). \quad (2.11)$$

Had $w_0(\mathbf{k}, \mathbf{q})$ consisted of a local contribution only, it would have been rather easy to find $w(\mathbf{k}, \mathbf{q})$ simply by dividing $w_0(\mathbf{k}, \mathbf{q})$ by the Hartree dielectric function $\epsilon(q)$ given by

$$\begin{aligned} \epsilon(q) &= 1 - \frac{4}{\pi^2 q^2} \int_{k \leq k_F} \frac{d^3 k}{k^2 - |\mathbf{k} + \mathbf{q}|^2} \\ &= 1 + \frac{2k_F}{\pi q^2} \left(\frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| + 1 \right). \end{aligned} \quad (2.12)$$

In the present case, however, $w_1(q)$ is given by

$$w_1(q) = \frac{4}{\pi^2 \epsilon(q) q^2} \int_{k \leq k_F} \frac{w_0(\mathbf{k}, \mathbf{q})}{k^2 - |\mathbf{k} + \mathbf{q}|^2} d^3 k. \quad (2.13)$$

Substituting for $w_0(\mathbf{k}, \mathbf{q})$ from (2.7), one obtains

$$w_1(q) = \frac{1 - \epsilon(q)}{\epsilon(q)} [v(q) + v_d(q)] + g(q), \quad (2.14)$$

where $g(q)$ is given by

$$g(q) = \frac{4}{\pi^2 \epsilon(q) q^2} \int_{k \leq k_F} \frac{f(\mathbf{k}, \mathbf{q})}{k^2 - |\mathbf{k} + \mathbf{q}|^2} d^3 k. \quad (2.15)$$

The screened form factor is now explicitly given by

$$w(\mathbf{k}, \mathbf{q}) = [v(q) + v_d(q)]/\epsilon(q) + f(\mathbf{k}, \mathbf{q}) + g(q). \quad (2.16)$$

It should be pointed out that all the assumptions and approximations intrinsic in Harrison's formalism are implicitly taken for granted in this calculation. Of these, it would be, perhaps, of significance for what follows to mention the assumption that the potential $W_0(r)$ can be expressed as a sum of pair potentials of ions. Such an assumption *a priori* excludes interactions of more complicated nature, such as many-body forces and exchange interactions between neighboring ions. The main benefit from this assumption is the possibility of writing the Fourier-transformed potential as a lattice sum of products of form and structure factors. The first comprises the physical contents of the problem, whereas the latter includes structural information only. This so-called diffraction model is already inherent in our calculations, where $w(\mathbf{k}, \mathbf{q})$ plays the role of the (screened) form factor.

In order to be able to compute phonon-dispersion relations, we need still another function, the so-called energy-wave-number characteristic $F(q)$. This function is obtained rigorously by Harrison¹⁹ and by Shaw,²³⁻²⁵ and here we only indicate its origin and meaning. Recall-

²³ The derivation of $F(q)$ is thoroughly discussed R. W. Shaw J. Phys. C (to be published).

²⁴ R. W. Shaw, Jr., Stanford University Report, 1968 (unpublished). This report contains a description of the numerical computations, a computer code, and listings of results for eight metals.

²⁵ R. W. Shaw, Jr., thesis, Microwave Laboratory Report No. 1666, Stanford University, 1968 (unpublished).

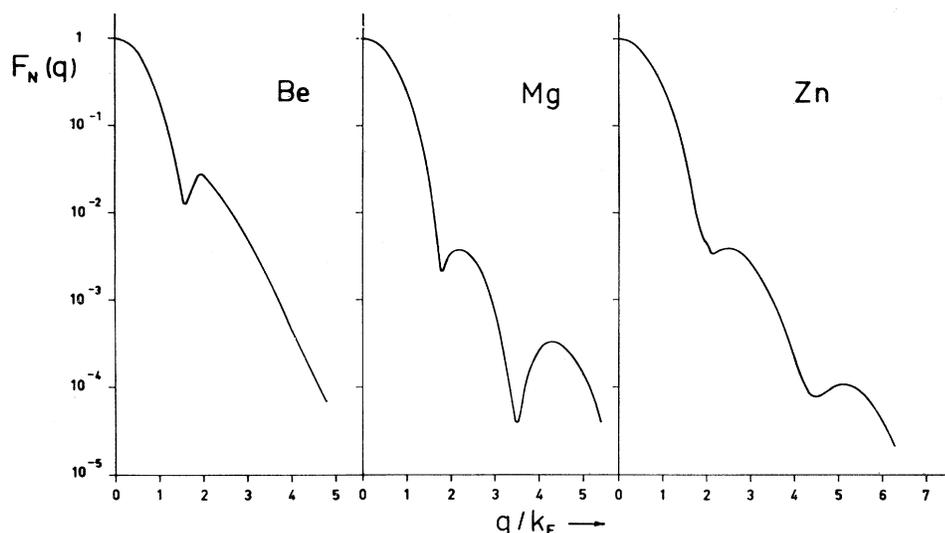


FIG. 1. Normalized energy-wave-number characteristics $F_N(q)$ for Be, Mg, and Zn. Note the logarithmic scale for the vertical axis.

ing that the main idea behind the pseudopotential approach is to obtain an effective potential that can be treated as a small perturbation in the Hamiltonian of the conduction electron with respect to the kinetic energy, one performs a perturbation expansion of the energy $E(k)$ and stops after the second-order contribution. This term is the lowest one in the expansion that contains scattering contributions of the electrons from the state \mathbf{k} to $\mathbf{k}+\mathbf{q}$. One then treats this term in the diffraction model¹⁹ by separating each term in the sum over \mathbf{q} to form and structure factors, respectively. The form factor is the function $F(q)$ that we need for our calculation, and is given by

$$F(q) = \frac{4\Omega_0}{(2\pi)^3} \int_{k \leq k_F} \frac{|w(\mathbf{k}, \mathbf{q})|^2}{k^2 - |\mathbf{k} + \mathbf{q}|^2} d^3k - \frac{\Omega_0 q^2}{8\pi} |w_1(q)|^2. \quad (2.17)$$

Given $w(\mathbf{k}, \mathbf{q})$ and $w_1(q)$, the computation of $F(q)$, though tedious, is straightforward. For the present calculations we choose these functions to be given by the optimum model potential of Shaw,²¹ that is, by Eqs. (2.14) and (2.16).

Although we postpone the discussion of the theoretical background for the computation of the phonon dynamical matrix until Sec. IV, it ought to be mentioned here that, in principle, our task of calculating the pseudopotential for this purpose is accomplished with the derivation of $F(q)$. This function contains all the information that one can obtain within the framework of the present theory about the effect of the conduction electrons on lattice dynamics in simple metals. $F(q)$ has the property that it diverges like $1/q^2$ as $q \rightarrow 0$. For this reason, it might be more convenient to represent $F(q)$ in a different form as suggested by Shaw.²⁴ Let $F_N(q)$ be set $F_N(0) = 1$, and be referred to as the normalized

energy-wave-number characteristics; then $F(q)$ is given via $F_N(q)$, and vice versa by

$$F_N(q) = -(\Omega_0 q^2 / 2\pi Z^{*2}) F(q). \quad (2.18)$$

Before concluding this section, there are two more points to which we would like to draw attention. The first involves the problem of how to include exchange and correlation of free electrons in the present calculations. As is well known, this problem is yet largely unsolved, and only crude estimates exist to account for these effects in the calculations of $\epsilon(q)$. Therefore, we do not attempt to include this effect in the present calculation. It should be mentioned, perhaps, that HAA¹⁴⁻¹⁷ include exchange and correlation in the spirit of Hubbard²⁶ in their expression for $\epsilon(q)$.

The second point that we would like to discuss briefly is the influence of the effective mass m^* of the electron on the present computations. The fact that $m^* \neq 1$ will be reflected in the screening properties of the conduction electrons, and one can readily account for this in the present formalism. The only way m^* enters this formulation is via the energy-wave-number relation, i.e.,

$$E = k^2 / 2m^*. \quad (2.19)$$

This means that whenever a perturbation summation occurs, the energy differences $E(k) - E(k')$ must be rescaled with respect to k , in accordance with (2.19). It can also be deduced that the nonlocal part $w(k, q)$ is not affected²⁷ by employing $m^* \neq 1$. Let us, therefore, denote quantities affected by $m^* \neq 1$ by a subscript m^* . Then $\epsilon_{m^*}(q)$ is given by

$$\epsilon_{m^*}(q) = 1 + m^* [\epsilon(q) - 1]. \quad (2.20)$$

²⁶ J. Hubbard, Proc. Roy. Soc. (London) A240 539 (1957); A243, 336 (1958).

²⁷ The energy-dependent functions $A_1(E)$ do not depend on m^* . This can be deduced from Eq. (2.1) after a little reflection.

TABLE I. Various constants used in the present calculations. Whenever not otherwise specified, the units are a.u.

	at. M wt	a (Å)	c (Å)	Ω_0	k_F	Z^{*a}	m^{*b}	$A_0^{a,c}$	$A_1^{a,c}$	$A_2^{a,c}$	$(\partial A_0/\partial E)_{EF}^a$	$(\partial A_1/\partial E)_{EF}^a$	$(\partial A_2/\partial E)_{EF}^a$
Be	9.013	2.281	3.577	54.36	1.0289	2.1244	1.05	1.000	0	0	-0.202	0	0
Mg	24.312	3.2028	5.1998	156.07	0.7239	2.1514	1.20	0.776	0.912	0	-0.286	-0.058	0
Zn	65.37	2.6648	4.9467	102.16	0.8338	2.1461	1.17	0.984	1.380	0.860	-0.355	-0.484	0

^a See Ref. 21.^b See Ref. 29.^c See Ref. 17.

Likewise, from Eq. (2.14), $w_{1m^*}(q)$ should be given by

$$w_{1m^*}(q) = \frac{m^* \epsilon(q)}{\epsilon_{m^*}(q)} w_1(q). \quad (2.21)$$

$w_{m^*}(k, q)$ and $F_{m^*}(q)$ can also be readily obtained through Eqs. (2.12) and (2.17).

III. NUMERICAL CALCULATION OF $F_N(q)$

Given the theory outlined in Sec. II, it is now possible to obtain numerical values for $F(q)$, or rather for $F_N(q)$. Before resorting to numerical calculation, it would be profitable to perform a few transformations of variables in order to obtain more convenient expressions. These substitutions have been proposed by Harrison¹⁹ and actually employed by Shaw.²³⁻²⁵ We define a set of new variables η , z , and v as

$$\eta = q/k_F, \quad z = k_{11}/k_F, \quad v = k_{\perp}/k_F, \quad (3.1)$$

where k_{11} and k_{\perp} represent, respectively, the parallel and perpendicular components of \mathbf{k} with respect to \mathbf{q} . The major part of the computation involves integration over the Fermi sphere that occurs in the evaluation of $g(q)$. Making the above substitutions, these integrals can be expressed in the following forms:

$$g(\eta) = \frac{8}{\pi k_F \eta^3 \epsilon(\eta)} \int_{-1}^1 \frac{dz}{2z + \eta} \int_0^{(1-z^2)^{1/2}} f(v, z, \eta) v dv, \quad (3.2)$$

$$F(\eta) = -\frac{\Omega_0 k_F}{\pi^2 \eta} \int_{-1}^1 \frac{dz}{2z + \eta} \int_0^{(1-z^2)^{1/2}} w^2(v, z, \eta) v dv - (\Omega_0 k_F^2 \eta^2 / 8\pi) w_1^2(\eta). \quad (3.3)$$

These expressions are more accessible to numerical calculations. Care must be taken, however, in properly treating²³ the singularity occurring at $z = -\frac{1}{2}\eta$.

All the numerical computations described in this paper²³ were performed on the IBM 360/65 computer situated at C.C.R., Euratom, Ispra. Although we use essentially the same procedure as Shaw,²³ there are some minor differences in the numerical techniques employed. This might give rise to some small numerical deviations of Shaw's results²¹ with respect to ours. We performed the calculations of $w(\mathbf{k}, \mathbf{q})$ for Be, Mg, and

Zn. For the case of Be and Mg, our results agree with Shaw's numbers to better than 1%. The relative agreement is perhaps not as striking as the absolute agreement, the latter being of the order of 10^{-5} . This makes the relative agreement excellent for large values of $w|(\mathbf{k}_F, \mathbf{q})|$, while for small $|w(\mathbf{k}_F, \mathbf{q})|$ the relative agreement remains 1%. In view of the approximations inherent in the theory, and inaccuracies occurring in the different numerical techniques employed, these deviations are definitely insignificant. The function $F_N(q)$ was calculated for the same metals, and the agreement with Shaw's data²³ is similar to that of $w(\mathbf{k}, \mathbf{q})$. In Fig. 1 we present the graphical results of $F_N(q)$ for Be, Mg, and Zn. In order to cope with the wide range of orders of magnitude spanned by $F_N(q)$, we use a logarithmic vertical scale. These numerical results are later used for the computations described in Sec. IV.

In addition to $F_N(q)$, we made another set of computations, where the effective mass of the electron, m^* , was different from 1. The data for m^* are taken from Weaire²⁹ and included in Table I. The difference between $F_{Nm^*}(q)$ and $F_N(q)$ is quite significant, but is still too small to show up in Fig. 1. In Table I we list the numerical parameters and constants pertinent to the present calculations.

IV. LATTICE DYNAMICS

In constructing the phonon dynamical matrix, we follow the customary approach of expressing the matrix elements as a sum of three contributions, namely,

$$\mathbf{D}(\mathbf{q}) = \mathbf{D}^R + \mathbf{D}^C + \mathbf{D}^E, \quad (4.1)$$

where the superscripts R , C , and E symbolize the core repulsion, Coulomb, and electronic contributions, respectively. First we try to justify the neglect of \mathbf{D}^R , which arises from overlap interaction between core electrons of nearest-neighbor ions.

Very little is known of how to obtain reliable estimates of this interaction by derivation from first principles. Moreover, in the framework of the present theory, it is required that the effective potential may be expressible as a sum of pair potentials, which might not be the case if core-repulsion interactions are present. It is hoped, therefore, that these interactions are small—in fact, negligibly small. Estimates of ion radii³⁰ for the ions of

²⁹ D. Weaire, J. Phys. C1, 210 (1968).²⁸ A report describing the FORTRAN IV programs that were used in these computations is under preparation and will be mailed on request by the authors as soon as it is available.³⁰ L. Pauling, J. Am. Chem. Soc. 49, 765 (1927); see also *Handbook of Chemistry and Physics*, (The Chemical Rubber Publishing Co., Cleveland, 1967/68), 48th ed., p. F-143.

Be^{2+} , Mg^{2+} , and Zn^{2+} are considerably smaller than half of the respective interionic distances in these metals, and thus it is believed that there is justification for this assumption and \mathbf{D}^E is, therefore, neglected in (4.1). This point, however, is further discussed in Sec. VI. Before proceeding to discuss and evaluate the remaining two contributions \mathbf{D}^C and \mathbf{D}^E , it would be worthwhile to elaborate further on some general properties of the phonon dynamical matrix. The reason for this is that we are dealing with crystals possessing more than one atom in their primitive unit cell. This fact calls for some caution when writing down the expressions for the dynamical matrix. Let $D_{\alpha\beta}(\kappa\kappa', \mathbf{q})$ represent a general element of the dynamical matrix, where $\alpha, \beta = x, y, z$ are the Cartesian coordinates, and $\kappa, \kappa' = 1, 2, \dots, n$ label the different n atoms in the unit cell, where for the present case $n=2$. The matrix elements can be written in the general framework of the Born-von Kármán theory as

$$D_{\alpha\beta}(\kappa\kappa', \mathbf{q}) = (M_\kappa M_{\kappa'})^{-1/2} \sum_l \Phi_{\alpha\beta}(l\kappa, l'\kappa') \times \exp\{i\mathbf{q} \cdot [\mathbf{r}(l) - \mathbf{r}(l')]\}, \quad (4.2)$$

where $\Phi_{\alpha\beta}(l\kappa, l'\kappa')$ is the (α, β) component of the force-constant tensor of an atom situated at (l, κ) with respect to an atom at (l', κ') , where $\mathbf{r}(l)$ and $\mathbf{r}(l')$ are lattice points. M_κ is the mass of the κ th atom. We adopt here the notation used by Maradudin *et al.*³¹ Owing to translational symmetry, $\Phi_{\alpha\beta}(l\kappa, l'\kappa')$ do not depend on l or l' , but only on their difference $l-l'$. Because of general properties of invariance under arbitrary translation, the force constants must satisfy the relation³¹

$$\sum_{l'\kappa'} \Phi_{\alpha\beta}(l\kappa, l'\kappa') = 0. \quad (4.3)$$

Equation (4.2) includes terms for which $l-l'=0$ and $\kappa=\kappa'$. Such terms, which would be interactions of atoms with themselves, obtain their meaning from Eq. (4.3),

and are, as a matter of fact, the reaction of an atom to the force exerted upon it by the crystal as a whole. Because of mathematical difficulties, it would be desirable to avoid such terms, and this can be easily achieved by subtracting (4.3) from (4.2). When doing so, we also set $l'=0$ for the sake of simplicity, and obtain

$$D_{\alpha\beta}(\kappa\kappa, \mathbf{q}) = \frac{1}{M_\kappa} \sum_l \Phi_{\alpha\beta}(l\kappa, 0\kappa) (e^{i\mathbf{q} \cdot \mathbf{r}(l)} - 1) - \frac{1}{M_\kappa} \sum_{l\kappa \neq \kappa'} \Phi_{\alpha\beta}(l\kappa, 0\kappa'), \quad (4.4)$$

while for $\kappa \neq \kappa'$ we retain the form of (4.2) with $l'=0$.

Eq. (4.4), though appearing to be less simple than (4.2), is by far more convenient, since it avoids the term $\Phi_{\alpha\beta}(0\kappa, 0\kappa)$. There is still another reason which is more practical for favoring Eq. (4.4). In our computation and, in fact, in any calculation, we make some approximations and practically never sum over all the force constants of the crystal. Equation (4.4) automatically guarantees, in this case, that crystal equilibrium exists no matter how poor the approximation may be. In other words, if we let $q \rightarrow 0$, Eq. (4.4) ensures that there still exist three acoustic modes with frequency tending to zero, whereas with (4.2) no such behavior necessarily occurs.

We now turn to the problem of evaluating \mathbf{D}^C and \mathbf{D}^E . The Coulomb part \mathbf{D}^C representing electrostatic interaction between bare ions can be expressed by employing Ewald's method for lattice sums as described by Kellermann.³² The detailed expressions for \mathbf{D}^C have been worked out by RV,⁷ but not in the spirit of Eq. (4.4). In a subsequent addendum,⁸ RV modified the expressions for \mathbf{D}^C and they are compatible with (4.4). In writing the expression for \mathbf{D}^C , we use much the same notation as RV, but we use atomic units rather than the conventional cgs units.

$$D_{\alpha\beta}^C(\kappa\kappa, \mathbf{q}) = \frac{2\pi Z^{*2}}{\Omega_0 M} \left[\sum_{\boldsymbol{\tau}} \frac{(\boldsymbol{\tau} + \mathbf{q})_\alpha (\boldsymbol{\tau} + \mathbf{q})_\beta}{|\boldsymbol{\tau} + \mathbf{q}|^2} \exp\left(-\frac{|\boldsymbol{\tau} + \mathbf{q}|^2}{4\eta^2}\right) - \sum_{\boldsymbol{\tau}'} \frac{\tau_\alpha \tau_\beta}{\tau^2} \exp\left(\frac{-\tau^2}{4\eta^2}\right) (1 + \cos \boldsymbol{\tau} \cdot \mathbf{R}_{12}) \right] + \frac{Z^{*2}}{M} \sum_l (e^{i\mathbf{q} \cdot \mathbf{r}(l\kappa)} - 1) \left[\left(\frac{\text{erfc}(\eta |\mathbf{r}(l\kappa)|)}{|\mathbf{r}(l\kappa)|^3} + \frac{2\eta \exp(-\eta^2 |\mathbf{r}(l\kappa)|^2)}{\sqrt{\pi} |\mathbf{r}(l\kappa)|^2} \right) \delta_{\alpha\beta} - \frac{[\mathbf{r}(l\kappa)]_\alpha [\mathbf{r}(l\kappa)]_\beta}{|\mathbf{r}(l\kappa)|^2} \left(\frac{3 \text{erfc}(\eta |\mathbf{r}(l\kappa)|)}{|\mathbf{r}(l\kappa)|^3} + \frac{6\eta \exp(-\eta^2 |\mathbf{r}(l\kappa)|^2)}{\sqrt{\pi} |\mathbf{r}(l\kappa)|^2} + \frac{4\eta^3 \exp(-\eta^2 |\mathbf{r}(l\kappa)|^2)}{\sqrt{\pi}} \right) \right] - \frac{Z^{*2}}{M} \sum_{l'} \left[\left(\frac{\text{erfc}(\eta |\mathbf{r}(l\kappa')|)}{|\mathbf{r}(l\kappa')|^3} + \frac{2\eta \exp(-\eta^2 |\mathbf{r}(l\kappa')|^2)}{\sqrt{\pi} |\mathbf{r}(l\kappa')|^2} \right) \delta_{\alpha\beta} - \frac{[\mathbf{r}(l\kappa')]_\alpha [\mathbf{r}(l\kappa')]_\beta}{|\mathbf{r}(l\kappa')|} \left(\frac{3 \text{erfc}(\eta |\mathbf{r}(l\kappa')|)}{|\mathbf{r}(l\kappa')|^3} + \frac{6\eta \exp(-\eta^2 |\mathbf{r}(l\kappa')|^2)}{\sqrt{\pi} |\mathbf{r}(l\kappa')|^2} + \frac{4\eta^3 \exp(-\eta^2 |\mathbf{r}(l\kappa')|^2)}{\sqrt{\pi}} \right) \right], \quad (4.5)$$

³¹ A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

³² E. W. Kellermann, *Phil. Trans. Roy. Soc. London A238*, 513 (1940).

$$\begin{aligned}
D_{\alpha\beta}^C(\kappa \neq \kappa', \mathbf{q}) = & \frac{2\pi Z^{*2}}{\Omega_0 M} \sum_{\boldsymbol{\tau}} \frac{(\boldsymbol{\tau} + \mathbf{q})_{\alpha} (\boldsymbol{\tau} + \mathbf{q})_{\beta}}{|\boldsymbol{\tau} + \mathbf{q}|^2} \exp(-|\boldsymbol{\tau} + \mathbf{q}|^2/4\eta^2) e^{-i\boldsymbol{\tau} \cdot \mathbf{R}_{12}} \\
& + \frac{Z^{*2}}{M} \sum_l \left[\left(\frac{\text{erfc}(\eta |\mathbf{r}(l\kappa\kappa')|)}{|\mathbf{r}(l\kappa\kappa')|^3} + \frac{2\eta \exp(-\eta^2 |\mathbf{r}(l\kappa\kappa')|^2)}{\sqrt{\pi} |\mathbf{r}(l\kappa\kappa')|^2} \right) \delta_{\alpha\beta} - \frac{[\mathbf{r}(l\kappa\kappa')]_{\alpha} [\mathbf{r}(l\kappa\kappa')]_{\beta}}{|\mathbf{r}(l\kappa\kappa')|^2} \left(\frac{3 \text{erfc}(\eta |\mathbf{r}(l\kappa\kappa')|)}{|\mathbf{r}(l\kappa\kappa')|^3} \right. \right. \\
& \left. \left. + \frac{6\eta \exp(-\eta^2 |\mathbf{r}(l\kappa\kappa')|^2)}{\sqrt{\pi} |\mathbf{r}(l\kappa\kappa')|^2} + \frac{4\eta^3}{\sqrt{\pi}} \exp(-\eta^2 |\mathbf{r}(l\kappa\kappa')|^2) \right) \right] e^{i\mathbf{q} \cdot \boldsymbol{\tau}(l\kappa\kappa')}. \quad (4.6)
\end{aligned}$$

In these expressions, $\boldsymbol{\tau}$ is a reciprocal lattice vector, η is a convergence parameter (not to be confused with the η used in Sec. III), \mathbf{R}_{12} is the distance vector between the two atoms in the unit cell in the hcp structure, $\mathbf{r}(l\kappa)$ is the vector position of the (l, κ) atom, $\mathbf{r}(l\kappa\kappa')$ is given by

$$\mathbf{r}(l\kappa\kappa') = \mathbf{r}(l\kappa) + \mathbf{R}_{\kappa\kappa'}, \quad (4.7)$$

and

$$\text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy. \quad (4.8)$$

In deriving \mathbf{D}^E we exactly follow the method of RV.⁷ Since nothing new is added to it here, we satisfy ourselves with merely indicating their method and quoting our final expression, which differs in a few respects from RV's expression. In obtaining \mathbf{D}^E , one may take advantage of Harrison's approach¹⁹ in employing structure factors and actually insert the lattice positions of the atoms in $S(\mathbf{q})$. In doing so, the instantaneous position of the atom as a function of time is used. Assuming that atomic displacements from equilibrium positions are small compared to interatomic distances, it is possible to expand the structure factor in a power series in these displacements, and make use of the harmonic approximation. After somewhat laborious manipulations, $D_{\alpha\beta}^E(\kappa\kappa', \mathbf{q})$ is expressed as a function of $F_N(q)$:

$$\begin{aligned}
D_{\alpha\beta}^E(\kappa\kappa, \mathbf{q}) = & -\frac{2\pi Z^{*2}}{\Omega_0 M} \sum_{\boldsymbol{\tau}} \left(\frac{(\boldsymbol{\tau} + \mathbf{q})_{\alpha} (\boldsymbol{\tau} + \mathbf{q})_{\beta}}{|\boldsymbol{\tau} + \mathbf{q}|^2} F_N(|\boldsymbol{\tau} + \mathbf{q}|) \right. \\
& \left. - \frac{\tau_{\alpha} \tau_{\beta}}{\tau^2} F_N(|\boldsymbol{\tau}|) (1 + \cos \boldsymbol{\tau} \cdot \mathbf{R}_{12}) \right), \quad (4.9)
\end{aligned}$$

$$\begin{aligned}
D_{\alpha\beta}^E(\kappa\kappa', \mathbf{q}) = & -\frac{2\pi Z^{*2}}{\Omega_0 M} \sum_{\boldsymbol{\tau}} \frac{(\boldsymbol{\tau} + \mathbf{q})_{\alpha} (\boldsymbol{\tau} + \mathbf{q})_{\beta}}{|\boldsymbol{\tau} + \mathbf{q}|^2} \\
& \times F_N(|\boldsymbol{\tau} + \mathbf{q}|) e^{i\boldsymbol{\tau} \cdot \mathbf{R}_{12}}. \quad (4.10)
\end{aligned}$$

On comparing our expressions for D^E with those of RV, we observe a few striking differences, but only one of them is truly significant. The trivial departures from RV's expressions are that we employ $F_N(q)$ rather than $F(q)$ [$E(q)$ in RV's notation] and that we express (4.9) and (4.10) in a somewhat more compact manner. The reason for employing $F_N(q)$ rather than $F(q)$ is that it is desirable to have a form factor that has the same value at $q=0$ for both the Coulomb and the electronic parts,

respectively. As a matter of fact, the function $e^{-q^2/4\eta^2}$ can be regarded as the form factor for the Coulomb part, and we obviously have

$$\lim_{q \rightarrow 0} e^{-q^2/4\eta^2} = \lim_{q \rightarrow 0} F_N(q) = 1. \quad (4.11)$$

The more serious departure from RV's expressions is in the coefficients of the sums in these expressions. The coefficient that appears in the RV paper is wrong, as can be clearly demonstrated via the following argument. Let $q \rightarrow 0$, and let us examine the behavior of $D_{\alpha\beta}^E(\kappa\kappa, \mathbf{q})$. The only term that does not tend to zero is the one with $\boldsymbol{\tau} = 0$ and $\alpha = \beta$, which indicates a LA mode. Since nevertheless $\mathbf{D}^C + \mathbf{D}^E$ must tend to zero as $q \rightarrow 0$, one has to look for exactly the same contribution but with opposite sign in $D_{\alpha\beta}^C(\kappa\kappa, \mathbf{q})$. This condition determines the coefficient of \mathbf{D}^E to be that given above. This point is also indicated by Harrison.¹⁹ Failure to adjust the coefficients of \mathbf{D}^C and \mathbf{D}^E in this manner leads to a divergence in the LA modes at $q=0$. This is presumably the reason why, in the RV paper, the LA mode along the $[0001]$ direction behaves peculiarly. In their addendum,⁸ RV implicitly corrected this error, as can be deduced from the graph of the same LA mode.

V. NUMERICAL COMPUTATIONS OF $\nu_j(q)$

Using the expressions for the dynamical matrix elements given in Sec. IV, a Fortran program was written²⁸ to calculate phonon-dispersion relations for Be, Mg, and Zn along high-symmetry directions: $\Delta(0,0,0,1)$, $\Sigma(1,0,1,0)$, T and $T'(1,1,2,0)$, and other directions. The numerical computations were performed on the IBM 360/65 computer at Euratom, Ispra. In all three cases of Be, Mg, and Zn, several different normalized energy-wave-number characteristics were tried. First we attempted to include exchange and correlation in a way similar to that of HAA. This effect on the dispersion relations $\nu_j(\mathbf{q})$ was of the order of 1% of the values of $\nu_j(\mathbf{q})$. The only appreciable effect that could be traced was the way it affected the slope of acoustic $\nu_j(\mathbf{q})$ at $q \sim 0$. This effect is mentioned by Harrison¹⁹ and can be visualized by analyzing its contribution to $\partial \nu_j / \partial q$ for which it is significant at $q \sim 0$, but its effect on ν_j itself is much less pronounced.

More noticeable than the above correction is the influence of varying m^* , the conduction electrons' effective mass. Here the difference in the phonon frequencies

Be

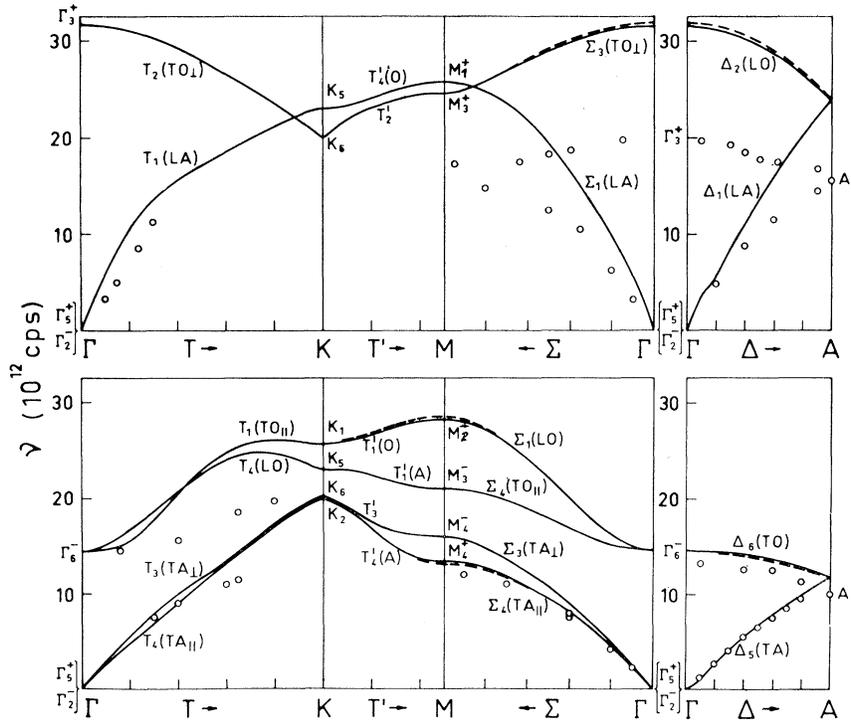


FIG. 2. Phonon-dispersion relations for Be. The dashed lines are calculated with unit effective mass; the solid line is for $m^* = 1.05$. The experimental data are sampled from Schmunk *et al.* (Ref. 11) for the Δ and Σ directions and from Schmunk (Ref. 33) for the T directions. The graphs are separated into two diagrams for clarity, as explained in the text.

could be as much as 10%. The values for m^* used in these computations were taken from Weaire.²⁹ We elaborate further on this in the separate description for each metal.

The accuracy of the calculations is better than 10^{-4} . A test of the precision is provided by the relation³² for the Coulomb part of the dynamical matrix, namely,

$$\sum_{\alpha} D_{\alpha\alpha}^c(\kappa\kappa, \mathbf{q}) = \frac{4\pi Z^{*2}}{\Omega_0 M} \quad (5.1)$$

and

$$\sum_{\alpha} D_{\alpha\alpha}^c(\kappa \neq \kappa', \mathbf{q}) = 0. \quad (5.2)$$

These relations are satisfied to an accuracy of 1 part in 10^4 . Further details of the computation are given individually for each metal.

A. Be

In calculating $\nu_j(\mathbf{q})$ for Be, the convergence parameter η for the Coulomb part was chosen to be $1.75/a$ (in \AA^{-1}), where a is the basal lattice parameter for Be. This number was found to give rapid convergence for the Coulomb lattice sum. The number of reciprocal lattice points used for the calculation of the electronic part was determined by the range of q for which $F_N(q)$ was significantly larger than zero [i.e., for $F_N(q) \geq 10^{-5}$]. In the case of Be, the range was $q/k_F = 6$, which corresponds to 403 different τ values. The number of neighbors in direct space was chosen to be 158. The results are shown

in Fig. 2. The dashed line represents the computation for which $m^* = 1$, and for the solid line $m^* = 1.05$. The experimental points are taken from Schmunk *et al.*¹¹ for the Δ and Σ directions and from Schmunk³³ for the T direction. In these experiments the time-of-flight technique was used for the measurement of inelastic coherent scattering of neutrons. In order to achieve more clarity in the presentation of the data, the graphs are split somewhat arbitrarily into two sets of dispersion relations. In the upper set we show LA modes as well as higher optic modes; in the lower set the four remaining branches are shown. The classification in terms of irreducible representations is according to Iyengar *et al.*³⁴ The disagreement between the experimental and calculated values of $\nu_j(\mathbf{q})$ is very striking in the upper graphs, the latter being some 60% higher. The situation is evidently better in the lower part of the graph, where the calculated values are only some 15% too high. Varying m^* did very little to improve the agreement. The over-all profile of the calculated dispersion relations much resembles that of BKH,¹⁰ the present results being some 10% lower than those of BKH. It might be of interest to compare the Γ_3^+ mode (LO mode at $q=0$) to the plasma frequency, given in cgs units by

$$\nu_p = Z^* e / (\pi \Omega_0 M)^{1/2}. \quad (5.3)$$

³³ R. E. Schmunk, Phys. Rev. **149**, 450 (1966).

³⁴ See Ref. 9; see also L. J. Raubenheimer and G. Gilat, Phys. Rev. **157**, 586 (1967) for a classification of the modes that are not treated in Ref. 9.

Mg

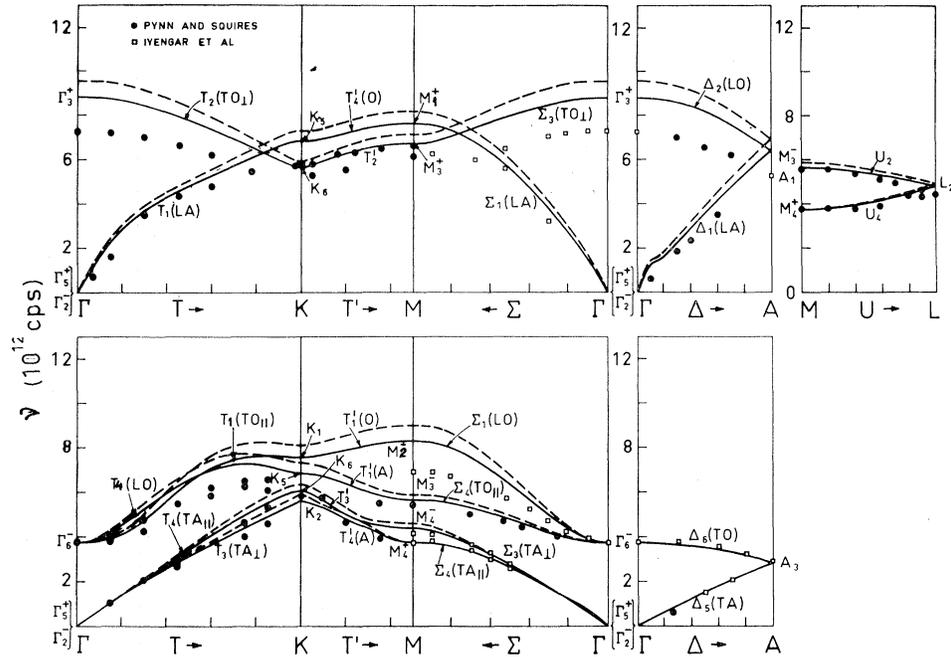


FIG. 3. Phonon-dispersion relations for Mg. Dashed lines are calculated for unit effective mass and for the solid lines $m^*=1.20$. Experimental data are sampled from Iyengar *et al.* (Ref. 9) and from Squires (Ref. 35) and Pynn and Squires (Ref. 36). The graphs are given in two parts for the sake of convenience, as explained in the text.

In the case of Be, $\nu_p = 52.3 \times 10^{12}$ cps and $\nu(\Gamma_3^+) = 31.9 \times 10^{12}$ cps for $m^*=1$, so that $\nu(\Gamma_3^+) = 0.61\nu_p$, which is a rather large fraction of ν_p .

B. Mg

The calculation of $\nu_j(\mathbf{q})$ for Mg was carried out along the same lines as for Be. The convergence factor η is $1.8/a(\text{\AA}^{-1})$. The range of the argument of $F_N(q)$ is $q/k_F = 7$, which corresponds to 245 different τ vectors. The number of neighbors in the direct lattice is 158. The graphical results for $\nu_j(\mathbf{q})$ are shown in Fig. 3; the dashed line corresponds to a unit effective mass, and the solid line to $m^*=1.20$. The experimental results for the inelastic scattering of neutrons are taken from papers by Iyengar *et al.*,⁹ who used the triple-axis spectrometer technique, and by Squires³⁵ and Pynn and Squires,³⁶ used time-of-flight technique. As in the case for Be, we represent the data in two sets of graphs. Also presented are two modes, U_2 and U_4 (see Ref. 34), along the U direction. The fit of calculated phonon frequencies to the measured ones is excellent for all TA modes. In these cases, varying m^* has very little effect on $\nu_j(\mathbf{q})$. For other modes, the agreement is less good. The worst agreement is found for longitudinal modes (upper part of Fig. 3), where the calculated values are about 30% higher than the observed frequencies. Upon setting $m^*=1.20$, the agreement improved somewhat, as can be

seen in Fig. 3. It is interesting to point out that our results agree very well with those of BKH, but are almost a factor of 2 higher than those of RV⁸ for the longitudinal modes. In the case of Mg, $\nu_p = 20.3 \times 10^{12}$ cps and $\nu(\Gamma_3^+) = 9.55 \times 10^{12}$ cps [for $m^*=1.20$, $\nu(\Gamma_3^+) = 8.81 \times 10^{12}$ cps]. The ratio $\gamma(\Gamma_3^+)/\nu_p = 0.47$ is better than for Be, but still relatively high. It was observed that the influence of m^* is to improve significantly the fit between calculation and experiment. We, therefore, tried to use m^* as an adjustable parameter and chose it to be $m^*=1.60$. In Fig. 4 we present the fit between experiment and the calculation including this one adjustable parameter. This fit proves to be excellent—much better than that obtained by RV,⁸ who used two adjustable parameters.

C. Zn

For Zn, we choose η to be $1.75/a(\text{\AA}^{-1})$. The range of q for $F_N(q)$ is $q/k_F = 7$, which corresponds to 417 different τ vectors. The number of neighbors is 134. Graphs for Zn are given in Fig. 5, in the same manner as for Be and Mg. Experimental results are taken from Borgonovi *et al.*,¹² who used the triple-axis spectrometer in their measurements. It is observed from Fig. 5 that although we still had three acoustic phonons at $\Gamma(q=0)$ (as is implied by the discussion in Sec. IV), there was a small range of wave vectors \mathbf{q} for which the model predicts imaginary frequencies for some of the acoustic modes. This implies that elastic constants predicted by the model are unrealistic. It should be added, though, that the absolute value of these frequencies is very small as compared to the range of frequencies shown in Fig. 5.

³⁵ G. L. Squires, Proc. Phys. Soc. (London) 88, 919 (1966).

³⁶ P. Pynn and G. L. Squires, in *Inelastic Scattering on Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1968), Vol. I, p. 215.

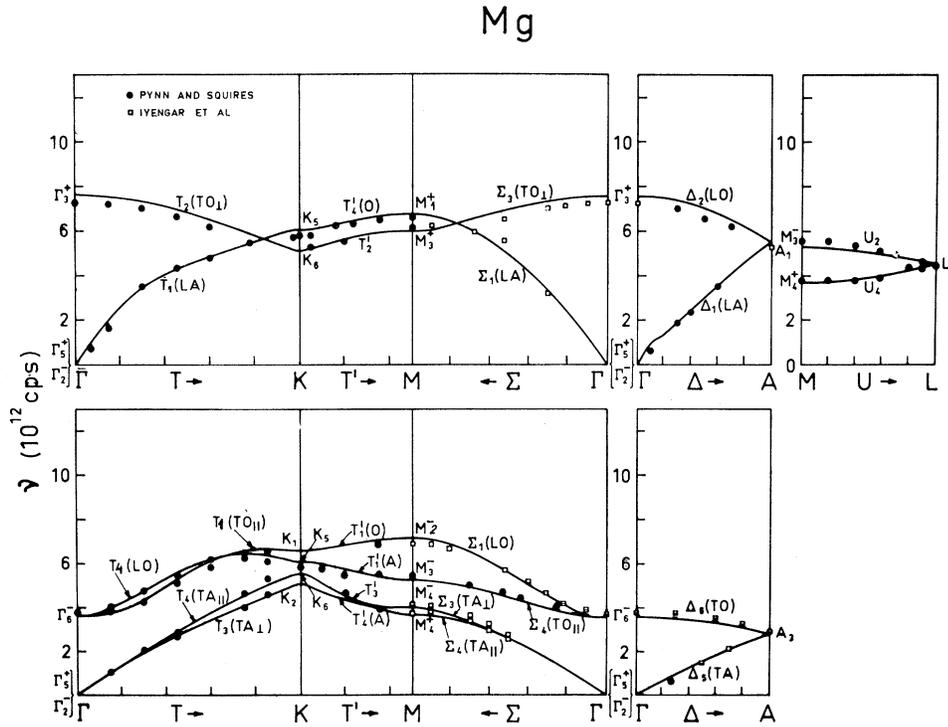


FIG. 4. Phonon-dispersion relations for Mg using $m^*=1.60$ as an adjusted parameter. Experimental data are the same as in Fig. 3.

Apart from this weak point of the model, it is surprising how good the fit to experimental results is for most of the optical branches, longitudinal as well as transverse. It is believed that the nonlocal contribution to the pseudopotential in Zn plays a much more significant role than in the cases of Be and Mg. This observation receives further support on comparing our calculations with those of BKH, who used a purely local pseudopotential. In their calculations, some of the branches are imaginary for most of the range of \mathbf{q} , and the absolute values for these imaginary frequencies is of the same order as the real frequencies.

The attempt to employ $m^*=1.17$ shifted the curves to some extent, as can be observed in Fig. 5; the over-all agreement to experimental results became slightly better as a result. It is possible that the value of $m^*=1.1$ as given by Animalu *et al.*¹⁷ might improve this agreement still further. In the case of Zn, we have $\nu_p=14.3 \times 10^{12}$ cps, compared to $\nu(\Gamma_3^+)=5.13 \times 10^{12}$ cps; and the ratio $\nu(\Gamma_3^+)/\nu_p=0.36$. It is of interest to point out that for $m^*=1.17$ we obtain $\nu(\Gamma_3^+)=4.35 \times 10^{12}$ cps. On setting $m^*=1.10$ and interpolating, we obtain $\nu(\Gamma_3^+)=4.67 \times 10^{12}$ cps, in excellent agreement with experiment.

VI. DISCUSSION AND SUMMARY

In trying to draw conclusions from the calculations described in this paper, it seems quite difficult to discuss the three metals simultaneously on the same footing. It will be much more useful if we discuss each metal individually. Nevertheless, before resorting to such a

discussion it would be worthwhile to make a few general remarks. Since the objective of this article is to try to calculate from first principles a reliable pseudopotential from which one could predict phonon-dispersion relations, we shall mainly concentrate on the question to what extent and why we fail or succeed in this project.

As was discussed earlier in this paper, computations prior to the present one^{7,8,10} were not very successful. One possible reason for this could be that in these calculations the pseudopotential was taken to be purely local. It seems to be the case, much to our disappointment, that the nonlocal part had a significant effect on phonon-dispersion relations only in the case of Zn. It can be concluded, therefore, that one ought to look elsewhere for explanations as to why one does not obtain good representation of data by applying pseudopotentials. One possible explanation was already pointed out by Kagan and Brovman,^{13,37} who use many-body techniques for the expansion of the electron energy. They find that among the terms entering this expansion are expressions representing three- (or more) body forces acting between ions via the conduction electrons. Each of these terms, however, contains a factor of the order of $(V/E_F)^{n-1}$, where V is an interaction energy of the order of magnitude of the pseudopotential interaction, and an n -body force is considered. Now $(V/E_F)^{n-1}$ can be considered as a factor of smallness, roughly being of

³⁷ Yu. Kagan and E. G. Brovman, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1968), Vol. I, p. 3. We are indebted to Dr. Kagan for sending us an English translation of this article.

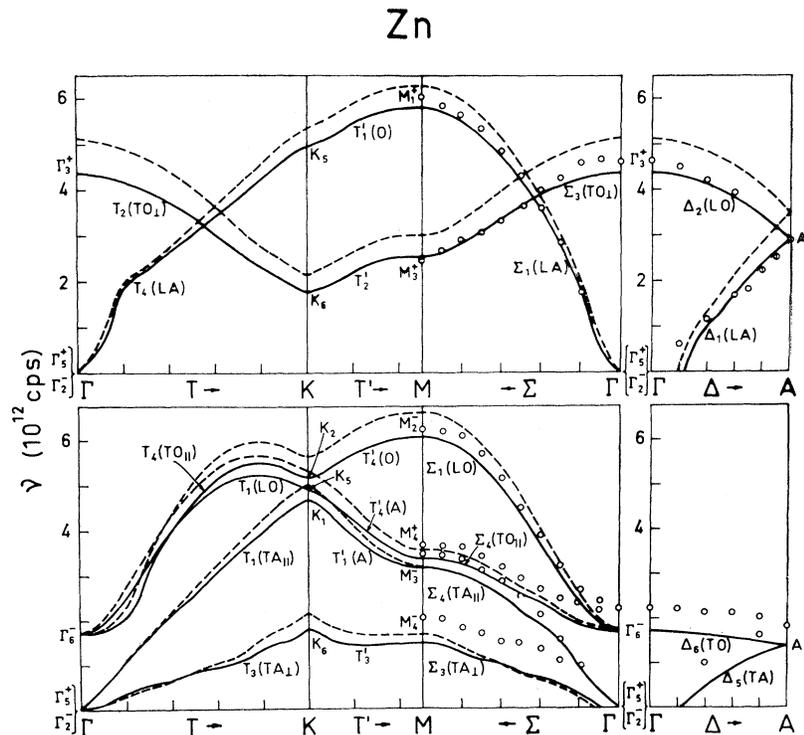


FIG. 5. Phonon-dispersion relations for Zn. Dashed lines are for unit effective mass and solid lines are for $m^* = 1.17$. Experimental data are taken from Borgonovi *et al.* (Ref. 12). For convenience, the graphs are given in two diagrams, as explained in the text.

the order of $10^{-(n-1)}$. Brovman and Kagan claim, therefore, that many-body forces should be rather negligible except for $n=3$ and for nearest-neighbor interactions only. If one accepts this argument at its face value, it means that the diffraction-model formalism set up by Harrison¹⁹ is no longer justifiable in a strict sense, since it explicitly assumes pair interactions between ions. It could still be salvaged, however, if these Brovman-Kagan forces could be considered as small perturbing interactions in comparison with the usual pair interactions. Recalling that in Sec. V we neglected overlap interactions between nearest neighbors, it seems to us that in view of the argument of Brovman and Kagan it is possible that forces between nearest neighbors might not be negligibly small, although they stem from other causes.

A second possible explanation for the partial failure of the pseudopotential approach was pointed out to us by Harrison,³⁸ and is concerned with the adequacy of second-order perturbations that one usually employs in these calculations. It is obvious that in computing properties such as phonon-dispersion relations in a metal which are, apart from the Coulomb terms, determined solely by this approximation, one should be aware of the error that is induced by neglecting higher-order perturbations. Now these higher-order contributions are not necessarily insignificant, and moreover, they depend, like the second-order perturbation, on the particular choice of the pseudopotential. A desirable choice of

a pseudopotential should therefore give an exact cancellation of the third-order terms to justify the use of the second-order approximation. There is, however, one snag in this approach, and it relates to the possibility that such a cancellation in calculating one property such as phonon-dispersion relations does not automatically imply cancellation of third-order contributions when another property is computed. One is therefore in need of certain adjustments in the pseudopotential approach that will guarantee that second-order perturbations be adequately correct for the purpose of calculating any relevant property.

Another possible factor which might have an effect on the present computation, but which is within the framework of the present theory, is the effect of the shape of the Fermi surface on screening. Obviously, in none of these metals do we encounter an ideal Fermi sphere, and yet in all these calculations we use a scalar dielectric function as well as integration over a sphere of radius k_F to obtain the appropriate screening field. It is hard to estimate how large an effect it would have if one used the appropriate shape of the Fermi surface for such integrations. This is, of course, a task which is almost impossible for practical reasons, and it will probably be long before anybody seriously attempts such a calculation. A crude way, however, to compensate for such shape effects of the Fermi surface (and the loss of the convenient concept of Fermi radius as a result), could be via the use of some average effective mass m^* . Physically, the effect of $m^* > 1$ is to increase the inertia of the electron gas and then cause a less efficient screen-

³⁸ W. A. Harrison (private communication).

ing of the model potential. This obviously results in a net increase in the negative contribution of the electronic part to the dynamical matrix, as is actually observed in the calculation. An m^* suitable to these calculations could be different from the average m^* predicted from other electronic properties of the metal. In this sense it might not be completely meaningless to try to use m^* as an adjustable parameter, as we actually did for Mg. In employing m^* as a free parameter, it should be noted that it can also implicitly account for many-body effects as well as higher-order perturbation corrections. We now discuss the individual results for each metal.

Be. The worst fit to the experimental data among the three present computations is for Be. It is perhaps not so surprising that this is the case, since the model potential has almost no inner structure for Be. This is so because Be^{2+} has only two $1s$ electrons, and therefore, its ionic core is spherically symmetric. This means that when expanding the plane wave in terms of s , p , and d waves, we get only the contribution of the s wave, which does not depend on the angle between \mathbf{k} and $\mathbf{k}+\mathbf{q}$. Physically this means that the Be^{2+} ions are treated by the model as perfect spheres with no inner structure, and all the model provides for is the radius of this sphere. A similar situation is probably encountered for Li^+ , and an attempt to find a reasonably good pseudopotential to represent the phonon data has failed so far.⁶ It is therefore believed that the nonlocal part of the model potential which essentially retains the inner structure of the ion cannot be of much significance, and this explains, perhaps, why our results fit so well those of BKH.¹¹ Employing $m^*=1.05$ rather than 1 also had very little effect on the results.

Mg. In the case of this metal, one would expect a greater contribution arising from the nonlocal part of the model potential. It is therefore all the more surprising how close our results happen to be to the BKH results. We are inclined, therefore, to conclude that in the case of Mg also, the nonlocal contribution to the model potential seems to be of secondary importance. On the other hand, it is found that for the case of Mg, varying the effective mass to $m^*=1.20$ had a very pronounced effect on improving the fit to the experimental data. The experimental value for m^* obtained from electronic-specific-heat data,³⁹ and supported by magnetoacoustic measurements⁴⁰ for Mg, is $m^*=1.33$. If we used this value in our computation, $\nu(\Gamma_3^+)$ would be equal to 8.31×10^{12} cps, in comparison with 7.30×10^{12} cps for the experimental value. By adjusting the value of $m^*=1.60$, we were able to obtain a very good fit indeed. Since our computation is for $T=0^\circ\text{K}$, and anharmonic effects are therefore neglected, we cannot hope

for better agreement with room temperature data. This good fit may, of course, be quite accidental and in any case $m^*=1.60$ seems to be too large a value. It is possible, therefore, that other corrections, such as exchange and correlation, are hidden in it. On the other hand, the fact that we were able to obtain such a good fit by employing only one adjustable parameter that does not play any essential role in the structure of the model, seems to us quite significant. As mentioned above, m^* could be regarded as some weighting factor compensating replacement of the Fermi surface by an equivalent sphere, and it is a property of the electron gas only. This success might cast some doubt on the assertion of Brovman and Kagan^{13,37} that many-body type forces should play an important role in the theory, since it is hardly conceivable that such an effect would be taken into account by using one free parameter only.

Zn. This metal is, much to our surprise, the only one of the three in which the optimum model potential could yield a fairly good agreement with experimental data. It is surprising because Zn is probably not as "simple" a metal as Mg. According to Shaw²¹ the energy band of the $3d$ state is very close to the Fermi level, and this makes a linear extrapolation of $A_1(E)$ to $A_1(E_F)$ quite dubious. We did so, nevertheless, in the absence of a better procedure. The result is that a somewhat dubious $F_N(q)$ for Zn provides a fairly good representation of the phonon spectrum of Zn. Another finding is that the non-local contribution to the potential is probably responsible for this relatively good fit. This can be deduced from comparing our results with those of BKH, who used an entirely local pseudopotential and were not able to obtain realistic results. Our calculations are also found to be sensitive to the value of m^* . Only in the case of Zn do we encounter, as BKH do, an instability of some of the acoustic modes near $q=0$. The reason for this instability is most probably associated with the unusually high c/a ratio of Zn. As a matter of fact, we actually tried to compute the phonon-dispersion relation for Zn, using the ideal $c/a=(8/3)^{1/2}$ with the same Ω_0 and $m^*=1$. The resultant $\nu_j(q)$ were appreciably different from those shown in Fig. 5: The longitudinal modes became much too high, and the transverse modes fitted the experimental results very well. However, the most significant result of this attempt was the complete disappearance of unstable modes from the phonon spectrum.

In conclusion, it might be said that although considerable progress has been made in the field of the pseudopotential theory of simple metals, one still needs a better theory that can predict phonon-dispersion relations at 0°K to within experimental error. As long as such a satisfactory theory does not exist, one could resort to empirical computation of $F_N(q)$ from phonon data, as demonstrated by Cochran³ for the case of Na or to adjust parameters as we do with m^* . Such empirical $F_N(q)$ could be helpful in computing other

³⁹ J. G. Duant, in *Process in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1955), p. 210.

⁴⁰ J. C. Kimball, P. W. Stark, and F. M. Mueller, *Phys. Rev.* **162**, 600 (1967).

electronic properties and might be of some help towards the development of a better theory.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. Robert W. Shaw, Jr. for providing us with results prior to publication and for his help and interest during the course of this work. We are also grateful to Professor Walter A. Harrison, Dr.

Yu. Kagan, and Dr. G. Venkataraman for their interest and their useful comments on the preliminary draft of the present paper. Two of the authors (G. G. and G. C.) wish to express their gratitude to the Comitato Nazionale per l'Energia Nucleare and to Professor G. Caglioti for the kind hospitality that they enjoyed at Ispra and for enabling them to carry out this project. We wish also to thank Professor G. Caglioti for his interest in this work and for many stimulating discussions

PHYSICAL REVIEW

VOLUME 185, NUMBER 3

15 SEPTEMBER 1969

Cohesive Force of Metals

G. H. WANNIER,* C. MISNER,† AND G. SCHAY, JR.‡
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
 (Received 11 March 1969)

If the Hellmann-Feynman theorem is applied to metals, using present-day Bloch-type functions, one finds a self-repulsion of the structure. A substantial concentration of electrons along the bonding directions is required if the self-repulsion is to be zero.

IN the course of a study of solid cohesion, we have come across a deficiency in present-day electronic wave functions for molecules and solids. It seems that the generalized force conjugate to a change in the lattice parameter does not come out equal to zero for the generally accepted wave functions, but has an appreciable value with the sign corresponding to self-repulsion.

If the generalized force opposing a deformation is computed by differentiation of the cohesive energy the above paragraph obviously is not correct. However, the force can be calculated directly by the use of a theorem of Hellmann¹ and of Feynman.² The calculation is even considerably simpler than the calculation of the energy because the theorem tells us that we may compute the force by simple electrostatics, treating the electrons as smeared out negative charges according to their wave functions.

If one works out from this theorem the generalized force $\partial U/\partial q$ opposing a lattice distortion in a simple crystal lattice of cubic symmetry one finds

$$\frac{\partial U}{\partial q} = \frac{1}{2} N e^2 \int_{\omega_0} [Z\delta(\mathbf{r}) - \rho(\mathbf{r})] \frac{\partial}{\partial q} \left[\sum'_{\mathbf{r}_i} \frac{1}{|\mathbf{r}_i - \mathbf{r}|} \right] d\mathbf{r}. \quad (1)$$

Here Ze is the nuclear charge, N the number of atoms in the crystal, $\rho(\mathbf{r})$ the electron density, q a parameter

measuring the lattice distortion, and ω_0 the Wigner-Seitz cell surrounding the one nucleus placed at the origin. The summation over \mathbf{r}_i proceeds over the lattice of all other nuclear positions. In taking the derivative with respect to q , we must treat only these quantities \mathbf{r}_i as dependent on that parameter.

Formula (1) implies that a charge distribution which is uniform or spherically symmetric within the Wigner-Seitz cell automatically leads to self-repulsion of the structure. This is because the total charge within the sphere inscribed in the cell acts as a slightly positive point charge placed at the center; the negative charge in the corners then forms a 16-pole with this central charge. The mutual orientation of these 16-poles is such as to lead to repulsion. We may verify this idea by adopting the following crude model for alkali metals: a spherically symmetrical core bearing one positive charge and not reaching the cell boundary, surrounded by a valence electron cloud distributed uniformly over the cell.³ For such a model, Eq. (1) is easily evaluated and yields

$$\partial U/\partial a = -(Ne^2/a^2) \times 0.045, \quad (2)$$

where a is the length of the elementary cube edge. We can convert this quantity to an internal pressure p . It equals

$$p = (e^2/a^4) \times 0.030. \quad (3a)$$

In lithium this number equals

$$p = 4800 \text{ atm}. \quad (3b)$$

* Permanent address: University of Oregon, Eugene, Ore.
 † Permanent address: University of Maryland, College Park, Md.
 ‡ Permanent address: University of Massachusetts, Boston, Mass.

¹ H. Hellmann, *Einführung in die Quantenchemie* (Franz Deuticke, Leipzig, 1937), p. 285.

² R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).

³ W. G. McMillan and A. L. Latter, *J. Chem. Phys.* **29**, 15 (1958). The model used here is a special case of the wider class of models proposed by them.