

## Lattice Dynamics of Magnesium Using a Pseudopotential Approach

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The lattice dynamics of hexagonal closed-packed metals is discussed using the pseudopotential approach of Harrison. Explicit expressions for the elements of the dynamical matrix are obtained and numerical calculations are made for the phonon dispersion relations along the [0001] and [0110] directions in magnesium, using the results previously obtained by Harrison from a first-principles calculation. Comparison with the experimental data of Iyengar *et al.*, however, shows poor agreement. Calculations are also made using a two-parameter-model pseudopotential proposed by Harrison, which shows better agreement with experiment.

### I. INTRODUCTION

THE availability in recent years of accurate experimental data on phonon dispersion relations in metals has stimulated considerable interest in their calculation from basic principles. The earliest work of this type is due to Toya,<sup>1</sup> who used the classic result of Bardeen<sup>2</sup> for electron-phonon interactions in sodium to compute the dispersion relations for that metal. The calculations were found to be in rather good agreement with experiment,<sup>3</sup> and later the method was used with suitable modifications to obtain the dispersion relations for lead<sup>4</sup> and copper.<sup>5-7</sup> A somewhat different approach based on the pseudopotential concept has been proposed by Sham.<sup>8</sup> Using a local as well as a nonlocal pseudopotential, calculations were made for sodium, and the agreement with experiment was as good as that obtained by Toya. The pseudopotential method has also been used by Harrison,<sup>9,10</sup> in a slightly different way, to compute dispersion relations for aluminium and lead. More recently, the dispersion relations for sodium, aluminium, and lead have been recalculated by Vosko *et al.*,<sup>11</sup> using a many-body treatment of screening, and the orthogonalized-plane-wave (OPW) method for evaluating the ion-electron matrix element. A notable feature of all the calculations which have been reported so far is that they are for metals which have just one atom per unit cell.

In this paper, we present some calculations of dispersion relations for magnesium—a metal with two

atoms per unit cell—using Harrison's approach. Two types of calculations are reported. In the first, the dispersion relations were obtained using Harrison's pseudopotential results<sup>9</sup> computed from first principles. The calculations show rather poor agreement with experimental results<sup>12</sup> obtained in this laboratory some time ago. The dispersion relations were then recalculated using a model pseudopotential,<sup>10</sup> the parameters of the model being determined by fitting to a few select experimentally measured frequencies. The latter results show much better agreement with experiment. The model pseudopotential thus derived should prove useful in computing various other properties of the metal.

Section II gives an account of the theoretical formulation. The numerical results obtained using the two approaches mentioned above, and a discussion of them, are presented in Sec. III.

### II. THEORETICAL FORMULATION

In this section we shall briefly review Harrison's approach and then give the expressions used in our calculations. The basic problem in computing phonon frequencies is to calculate the second-order change in energy of the crystal when the ions are displaced from their equilibrium positions. Harrison approaches this problem for metals with nearly free-electron behavior (of which Mg is an example) as follows. Starting with the one-electron Schrödinger equation

$$(T+V)\psi_{\mathbf{k}}=E_{\mathbf{k}}\psi_{\mathbf{k}},$$

where  $V$  is the self-consistent potential and  $\psi_{\mathbf{k}}$  is the Bloch wave (expressed in terms of OPW's) corresponding to energy  $E_{\mathbf{k}}$ , he goes over into a consideration of the pseudopotential equation

$$(T+W)\phi_{\mathbf{k}}=E_{\mathbf{k}}\phi_{\mathbf{k}}.$$

Here  $\phi_{\mathbf{k}}$  is a smooth and nearly free-electron-like function devoid of the rapid oscillations that occur in  $\psi_{\mathbf{k}}$  near the ion cores. If  $\phi_{\mathbf{k}}$  is to be nearly free-electron-like, then clearly the pseudo potential  $W$  must be small. It

<sup>1</sup> T. Toya, J. Res. Inst. Catalysis, Hokkaido Univ. **9**, 178 (1961).

<sup>2</sup> J. Bardeen, Phys. Rev. **52**, 688 (1937).

<sup>3</sup> A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. Bowers, Phys. Rev. **128**, 1112 (1962).

<sup>4</sup> T. Toya, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Ltd., Oxford, England, 1964), p. 91.

<sup>5</sup> T. Toya, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 25.

<sup>6</sup> P. L. Srivatsava and B. Dayal, Phys. Rev. **140**, A1014 (1965).

<sup>7</sup> S. K. Sinha, Phys. Rev. **143**, 422 (1966).

<sup>8</sup> L. J. Sham, Proc. Roy. Soc. (London) **A283**, 33 (1965).

<sup>9</sup> W. Harrison, Phys. Rev. **136**, A1107 (1964). See also T. Schneider and E. Stoll, Physik Kondensierten Materie **5**, 330 (1966).

<sup>10</sup> W. Harrison, Phys. Rev. **139**, A179 (1965).

<sup>11</sup> S. H. Vosko, R. Taylor, and G. H. Keech, Can. J. Phys. **43**, 1187 (1965).

<sup>12</sup> P. K. Iyengar, G. Venkataraman, P. R. Vijayaraghavan, and A. P. Roy, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 153.

has been pointed out by several authors<sup>13</sup> that there is a certain arbitrariness in  $\phi_k$  and, correspondingly, in  $W$ . Harrison uses this flexibility to choose a convenient form for  $W$  which leads to the smoothest  $\phi_k$  possible, and then obtained  $E_k$  via a perturbation approach, i.e.,

$$E_k = \frac{\hbar^2 k^2}{2m} + \langle \mathbf{k} | W | \mathbf{k} \rangle + \sum'_{\mathbf{q}} \frac{\langle \mathbf{k} | W | \mathbf{k} + \mathbf{q} \rangle \langle \mathbf{k} + \mathbf{q} | W | \mathbf{k} \rangle}{(\hbar^2/2m)[k^2 - (\mathbf{k} + \mathbf{q})^2]},$$

where  $|\mathbf{k}\rangle$ , etc., are plane waves, and the prime denotes the omission of the  $\mathbf{q} = 0$  term from the summation. Having obtained the one-electron energies in this fashion, Harrison next calculates the total (potential) energy of the crystal by first summing the one-electron energies over all states within the Fermi sphere. From this he subtracts the Coulomb self-energy of the conduction electrons (since it is counted twice in the Hartree approximation) and then adds the direct Coulomb interactions between the ions. The total energy obtained in this way is then regrouped into three terms:  $E_{fe}$ ,  $E_{es}$ , and  $E_{bs}$ . Of these,  $E_{fe}$ , called the free-electron energy, depends only on the density of the ions and not on their detailed arrangement.  $E_{es}$  is the electrostatic energy given by

$$E_{es} = \frac{1}{2} \sum_{i \neq j} (Z^* e)^2 / (|\mathbf{r}_i - \mathbf{r}_j|) + (\text{energy of interaction of ions with uniform compensating background}). \quad (1)$$

$Z^*$  is the effective valence, which is different from the true valence  $Z$  ( $= 2$  for Mg) because of effects connected with the orthogonalization of the conduction-electron wave function with core states.

The final term  $E_{bs}$  is referred to by Harrison as the band-structure energy. It is given by

$$E_{bs} = nNZ \sum'_{\mathbf{q}} S^*(\mathbf{q}) S(\mathbf{q}) E(\mathbf{q}). \quad (2)$$

$S(\mathbf{q})$  is the structure factor defined by

$$S(\mathbf{q}) = \frac{1}{Nn} \sum_{lk} \exp[-i\mathbf{q} \cdot \mathbf{r}(l, k)], \quad (3)$$

where  $n$  is the number of ions per primitive unit cell,  $N$  is the number of unit cells, and  $\mathbf{r}(l, k)$  is the position of the  $k$ th ion in the  $l$ th cell. If the ion is in its equilibrium position, then  $\mathbf{r}(l, k)$  will be given by

$$\mathbf{r}(l, k) = \mathbf{r}(l) + \mathbf{r}(k), \quad (4)$$

<sup>13</sup> See, for example, M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

where  $\mathbf{r}(l)$  denotes the position of the origin of the  $l$ th cell and  $\mathbf{r}(k)$  the equilibrium position of the  $k$ th ion with respect to that cell. The remaining quantity  $E(\mathbf{q})$ , called the energy-wave-number characteristic, depends only on the atomic volume  $\Omega_0$  and the pseudopotential. It has a simple physical meaning, as we shall see later. It is to be noted that there is no term in the potential energy associated with short-range repulsive forces arising from overlap of adjacent ions. This term is absent because the cores are assumed to be small, an assumption which is quite good in the case of magnesium.<sup>9</sup>

The problem of computing vibration spectra center on calculating the changes in the various contributions to the energy of the ion-electron system when the ions are displaced from their equilibrium positions. We shall, in what follows, confine our attention to ionic rearrangements at constant volume.<sup>14</sup> This means that  $E_{fe}$  can be dropped from further consideration, since it depends only on the volume and not on ionic positions.

Now it is well known in the theory of lattice dynamics that the change in potential energy of the crystal (up to second order in displacements of the ions) associated with a periodic disturbance of wave vector  $\mathbf{q}$  can be quite generally expressed as<sup>15</sup>

$$\frac{1}{2} \sum_{kk'} \sum_{\alpha\beta} [D_{\alpha\beta}(\mathbf{q}, kk') a_{\alpha}^*(\mathbf{q}, k) a_{\beta}(\mathbf{q}, k') + D_{\alpha\beta}^*(\mathbf{q}, kk') a_{\alpha}(\mathbf{q}, k) a_{\beta}^*(\mathbf{q}, k')]. \quad (5)$$

Here  $\mathbf{D}$  is the  $3n$ -dimensional dynamical matrix. The  $3n$  eigenvalues of this matrix give the squares of the  $3n$  vibrational frequencies associated with wave vector  $\mathbf{q}$ . The vector  $\mathbf{a}$  is an amplitude vector related to the displacement  $\mathbf{u}(l, k)$  of the atom  $(l, k)$  by

$$\mathbf{u}(l, k) = \frac{1}{(NM)^{1/2}} \{ \mathbf{a}(\mathbf{q}, k) \exp[i\mathbf{q} \cdot (\mathbf{r}(l) + \mathbf{r}(k))] + \mathbf{a}^*(\mathbf{q}, k) \exp[-i\mathbf{q} \cdot (\mathbf{r}(l) + \mathbf{r}(k))] \}, \quad (6)$$

where  $M$  is the mass of the ion (the crystal is assumed to be monatomic). In Eq. (6), we have to take both  $\mathbf{a}$  and  $\mathbf{a}^*$  into account in order to ensure that the displacement is real.

Since there are two contributions to the potential energy, namely,  $E_{es}$  and  $E_{bs}$ , there will correspondingly be two contributions to the dynamical matrix. Of these, that due to Coulomb interactions has been considered previously by Kellermann,<sup>16</sup> and the relevant ex-

<sup>14</sup> The limitations of such an approach have been discussed by Sham (Ref. 8).

<sup>15</sup> M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 173.

<sup>16</sup> E. W. Kellermann, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

pressions are as follows:

$$D_{\alpha\beta}^c(\mathbf{q}, k, k) = \frac{4\pi(Z^*e)^2}{n\Omega_0 M} \sum_{\boldsymbol{\tau}} \frac{(\boldsymbol{\tau}+\mathbf{q})_{\alpha}(\boldsymbol{\tau}+\mathbf{q})_{\beta}}{(\boldsymbol{\tau}+\mathbf{q})^2} \exp\left[-\frac{1}{4\eta^2}(\boldsymbol{\tau}+\mathbf{q})^2\right] + \frac{(Z^*e)^2}{M} \sum_l \left[ \left\{ \frac{\text{erfc}(\eta|\mathbf{r}(l, k)|)}{|\mathbf{r}(l, k)|^3} \right. \right. \\ \left. \left. + \frac{2\eta}{\sqrt{\pi}} \frac{\exp[-\eta^2|\mathbf{r}(l, k)|^2]}{|\mathbf{r}(l, k)|^2} \right\} \delta_{\alpha\beta} - \frac{[\mathbf{r}(l, k)]_{\alpha}[\mathbf{r}(l, k)]_{\beta}}{|\mathbf{r}(l, k)|^2} \left\{ \frac{3 \text{erfc}(\eta|\mathbf{r}(l, k)|)}{|\mathbf{r}(l, k)|^3} + \frac{6\eta}{\sqrt{\pi}} \frac{\exp[-\eta^2|\mathbf{r}(l, k)|^2]}{|\mathbf{r}(l, k)|^2} \right. \right. \\ \left. \left. + \frac{4\eta^3}{\sqrt{\pi}} \exp[-\eta^2|\mathbf{r}(l, k)|^2] \right\} \right] \exp[i\mathbf{q} \cdot \mathbf{r}(l, k)] - \frac{4(Z^*e)^2\eta^3}{3(\sqrt{\pi})M} \delta_{\alpha\beta} + \frac{4\pi}{3} \frac{(Z^*e)^2}{M\Omega_0} \delta_{\alpha\beta}, \quad (7)$$

$$D_{\alpha\beta}^c(\mathbf{q}, k, k') = \frac{4\pi(Z^*e)^2}{n\Omega_0 M} \sum_{\boldsymbol{\tau}} \frac{(\boldsymbol{\tau}+\mathbf{q})_{\alpha}(\boldsymbol{\tau}+\mathbf{q})_{\beta}}{(\boldsymbol{\tau}+\mathbf{q})^2} \exp\left[-\frac{1}{4\eta^2}(\boldsymbol{\tau}+\mathbf{q})^2\right] \exp[-i\boldsymbol{\tau} \cdot \mathbf{r}(k', k)] + \frac{(Z^*e)^2}{M} \\ \times \sum_{l'} \left[ \left\{ \frac{\text{erfc}(\eta|\mathbf{r}(l', k', k)|)}{|\mathbf{r}(l', k', k)|^3} + \frac{2\eta}{\sqrt{\pi}} \frac{\exp[-\eta^2|\mathbf{r}(l', k', k)|^2]}{|\mathbf{r}(l', k', k)|^2} \right\} \delta_{\alpha\beta} - \frac{[\mathbf{r}(l', k', k)]_{\alpha}[\mathbf{r}(l', k', k)]_{\beta}}{|\mathbf{r}(l', k', k)|^2} \left\{ \frac{3 \text{erfc}(\eta|\mathbf{r}(l', k', k)|)}{|\mathbf{r}(l', k', k)|^3} \right. \right. \\ \left. \left. + \frac{6\eta}{\sqrt{\pi}} \frac{\exp[-\eta^2|\mathbf{r}(l', k', k)|^2]}{|\mathbf{r}(l', k', k)|^2} + \frac{4\eta^3}{\sqrt{\pi}} \exp[-\eta^2|\mathbf{r}(l', k', k)|^2] \right\} \right] \exp[+i\mathbf{q} \cdot \mathbf{r}(l', k', k)]. \quad (8)$$

In the above equations, the various symbols have the following meanings:  $\boldsymbol{\tau}$  is a reciprocal lattice vector;  $r(k', k)$  is the distance of the  $k'$ th ion from the  $k$ th ion in a given cell, while  $\mathbf{r}(l', k', k)$  is the vector joining the  $k$ th ion in the unit cell at the origin to the  $k'$ th ion in the  $l'$ th cell. All distances in Eqs. (7) and (8) refer to the undistorted crystal.  $\text{erfc}(x)$  is the complementary error function of argument  $x$  defined by

$$\text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt.$$

The only difference between Kellermann's expressions and the ones given above is the term  $[4\pi(Z^*e)^2/3M\Omega_0]\delta_{\alpha\beta}$  in Eq. (7). This arises from the interactions between the ion and the uniform (nonresponsive) electron background. In Kellermann's case, since he was considering an ionic crystal, this term is absent. We follow Sham in including this contribution with the diagonal terms of the Coulomb coefficients. The quantity  $\eta$  is a parameter whose value is chosen such that the series converge rapidly both in real space and in reciprocal space.

The task of calculating the change in the band-structure energy and the contribution therefrom to the dynamical matrix still remains. In doing this, we note that the change in band-structure energy arises prima-

riarily from the change in the structure factor.<sup>17</sup>  $E(Q)$  does not change when the crystal is distorted at constant volume, since, as already remarked, it does not depend upon ionic positions. Consider now the structure factor  $S(\mathbf{Q})$  of the distorted crystal corresponding to a Fourier component  $\mathbf{Q}$ . This will be given say, by,

$$S(\mathbf{Q}) = \frac{1}{Nn} \sum_{lk} \exp[-i\mathbf{Q} \cdot \{\mathbf{r}(l) + \mathbf{r}(k) + \mathbf{u}(l, k)\}] \\ = \frac{1}{Nn} \sum_{lk} \exp[-i\mathbf{Q} \cdot \{\mathbf{r}(l) + \mathbf{r}(k)\}] \\ \times \left[ 1 - i\mathbf{Q} \cdot \mathbf{u}(l, k) - \frac{1}{2!} \{\mathbf{Q} \cdot \mathbf{u}(l, k)\}^2 + \dots \right] \\ = \sum_{j=0}^{\infty} S^j(Q), \quad (9)$$

where  $S^j(Q)$  denotes the contribution to  $S(Q)$  from the term involving the  $j$ th power of  $\mathbf{u}$ . Substituting for  $\mathbf{u}$  from Eq. (6) and using the result

$$\sum_l \exp[-i\mathbf{Q} \cdot \mathbf{r}(l)] = N\delta_{\mathbf{Q}, \boldsymbol{\tau}}, \quad (10)$$

it follows that

$$S^0(\mathbf{Q}) = \frac{1}{n} \sum_k \exp[-i\mathbf{Q} \cdot \mathbf{r}(k)] \delta_{\mathbf{Q}, \boldsymbol{\tau}},$$

$$S^1(\mathbf{Q}) = -\frac{i}{(NM)^{1/2}} \left[ -\sum_k \exp[-i(\mathbf{Q}-\mathbf{q}) \cdot \mathbf{r}(k)] \{\mathbf{Q} \cdot \mathbf{a}(\mathbf{q}, k)\} \delta_{(\mathbf{Q}-\mathbf{q}), \boldsymbol{\tau}} + \frac{1}{n} \sum_k \exp[-i(\mathbf{Q}+\mathbf{q}) \cdot \mathbf{r}(k)] \{\mathbf{Q} \cdot \mathbf{a}^*(\mathbf{q}, k)\} \delta_{(\mathbf{Q}+\mathbf{q}), \boldsymbol{\tau}} \right];$$

<sup>17</sup> W. Harrison, *Pseudopotential in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966), p. 42.

$$S^2(\mathbf{Q}) = \frac{1}{2NM} \left[ \frac{1}{n} \sum_k \exp[-i(\mathbf{Q}-2\mathbf{q}) \cdot \mathbf{r}(k)] \{ \mathbf{Q} \cdot \mathbf{a}(\mathbf{q}, k) \}^2 \delta_{(\mathbf{Q}-2\mathbf{q}), \tau} + \frac{1}{n} \sum_k \exp[-i(\mathbf{Q}+2\mathbf{q}) \cdot \mathbf{r}(k)] \right. \\ \left. \times \{ \mathbf{Q} \cdot \mathbf{a}^*(\mathbf{q}, k) \}^2 \delta_{(\mathbf{Q}+2\mathbf{q}), \tau} + \frac{2}{n} \sum_k \exp[-i\mathbf{Q} \cdot \mathbf{r}(k)] \{ \mathbf{Q} \cdot \mathbf{a}(\mathbf{q}, k) \} \{ \mathbf{Q} \cdot \mathbf{a}^*(\mathbf{q}, k) \} \delta_{\mathbf{Q}, \tau} \right]. \quad (11)$$

The higher-order terms are not of interest to us, since we shall be working in the harmonic approximation, which means that in the product  $S^*(\mathbf{Q})S(\mathbf{Q})$  we shall need only terms up to second order in  $\mathbf{a}$ .

We thus have

$$E_{\text{bs}}(\text{distorted}) - E_{\text{bs}}(\text{equilibrium}) = \delta E_{\text{bs}} = nNZ \sum_{\mathbf{Q}} [S^*(\mathbf{Q})S(\mathbf{Q})E(Q) - S^{*0}(\mathbf{Q})S^0(\mathbf{Q})E(Q)].$$

Using Eqs. (9)–(11) and retaining terms up to second order in  $\mathbf{a}$ , it is straightforward to show that<sup>17</sup>

$$\delta E_{\text{bs}} = \frac{Z}{nM} \left[ \sum_{\tau} \left\{ \left| \sum_k (\boldsymbol{\tau} + \mathbf{q}) \cdot \mathbf{a}^*(\mathbf{q}, k) \exp[i\boldsymbol{\tau} \cdot \mathbf{r}(k)] \right|^2 E(|\boldsymbol{\tau} + \mathbf{q}|) + \left| \sum_k (\boldsymbol{\tau} - \mathbf{q}) \cdot \mathbf{a}(\mathbf{q}, k) \right. \right. \right. \\ \left. \left. \times \exp[i\boldsymbol{\tau} \cdot \mathbf{r}(k)] \right|^2 E(|\boldsymbol{\tau} - \mathbf{q}|) - 2 \{ \boldsymbol{\tau} \cdot \mathbf{a}(\mathbf{q}, k) \} \{ \boldsymbol{\tau} \cdot \mathbf{a}^*(\mathbf{q}, k) \} F(k) E(|\boldsymbol{\tau}|) \right], \quad (12)$$

where

$$F(k) = \sum_{k'} \cos(\boldsymbol{\tau} \cdot \mathbf{r}(k'/k)).$$

Comparing with expression (5), we obtain finally for the electronic contribution to the dynamical matrix the following results:

$$D_{\alpha\beta}^E(\mathbf{q}, k, k) = \frac{Z}{nM} \sum_{\tau} [(\boldsymbol{\tau} + \mathbf{q})_{\alpha} (\boldsymbol{\tau} + \mathbf{q})_{\beta} E(|\boldsymbol{\tau} + \mathbf{q}|) + (\boldsymbol{\tau} - \mathbf{q})_{\alpha} (\boldsymbol{\tau} - \mathbf{q})_{\beta} E(|\boldsymbol{\tau} - \mathbf{q}|) - 2(\boldsymbol{\tau})_{\alpha} (\boldsymbol{\tau})_{\beta} F(k) E(|\boldsymbol{\tau}|)]; \quad (13)$$

$$D_{\alpha\beta}^E(\mathbf{q}, k, k') = \frac{Z}{nM} \sum_{\tau} [(\boldsymbol{\tau} + \mathbf{q})_{\alpha} (\boldsymbol{\tau} + \mathbf{q})_{\beta} \exp[-i\boldsymbol{\tau} \cdot \mathbf{r}(k'/k)] \\ \times E(|\boldsymbol{\tau} + \mathbf{q}|) + (\boldsymbol{\tau} - \mathbf{q})_{\alpha} (\boldsymbol{\tau} - \mathbf{q})_{\beta} \exp[i\boldsymbol{\tau} \cdot \mathbf{r}(k'/k)] E(|\boldsymbol{\tau} - \mathbf{q}|)]. \quad (14)$$

Note that in our formalism  $\mathbf{D}(\mathbf{q}, k, k)$  is real. In general, it is Hermitian.

The results given above can also be arrived at via a more conventional force-constant approach by noting the fact, pointed out by Harrison,<sup>18</sup> that there exists a central interatomic potential  $V(r)$ , say, of the form

$$V(r) = \frac{Z^* e^2}{r} + \frac{2Z}{N} \sum_{\mathbf{Q}} E(Q) \exp[i\mathbf{Q} \cdot \mathbf{r}] \\ = V^c(r) + V^E(r). \quad (15)$$

Introducing the Fourier representation of  $V(R)$  given by

$$V(R) = \frac{1}{nN\Omega_0} \sum_{\mathbf{Q}} V(Q) \exp[i\mathbf{Q} \cdot \mathbf{R}], \quad (16)$$

it immediately follows that

$$\frac{\partial^2 V}{\partial R_{\alpha} \partial R_{\beta}} = -\frac{1}{nN\Omega_0} \sum_{\mathbf{Q}} Q_{\alpha} Q_{\beta} V(Q) \exp[i\mathbf{Q} \cdot \mathbf{R}].$$

<sup>18</sup> W. A. Harrison, Phys. Rev. **129**, 2503 (1963).

Using this result in the familiar equation

$$D_{\alpha\beta}(\mathbf{q}, k, k') = \frac{1}{M} \sum_{l'} \left[ -\frac{\partial^2 V}{\partial R_{\alpha} \partial R_{\beta}} \right]_{\mathbf{R}=\mathbf{r}(l, k) - \mathbf{r}(l', k')} \\ \times \exp[-i\mathbf{q} \cdot \{ \mathbf{r}(l, k) - \mathbf{r}(l', k') \}],$$

the expressions given earlier for the elements of  $\mathbf{D}^E$  may be easily obtained. We might add that our expression for  $D_{\alpha\beta}^E(\mathbf{q}, k, k)$  reduces to that given earlier by other authors<sup>8, 11, 19</sup> for the case of crystals with one ion per unit cell.

Before concluding this section, we shall refer briefly to the physical significance of  $E(q)$ . From Eqs. (15) and (16), it is clear that  $E(q)$  is (apart from a constant) the Fourier transform of the ion-electron-ion potential  $V^E(r)$ . This has been pointed out earlier by Cochran.<sup>19</sup>

### III. NUMERICAL RESULTS AND DISCUSSIONS

The expressions given in Sec. II for the elements of the dynamical matrix have been programmed for com-

<sup>19</sup> W. Cochran, in *Inelastic Scattering of Neutrons in Liquids and Solids* (International Atomic Energy Agency, Vienna, 1965), Vol. I, p. 3.

TABLE I. Coulomb coefficients for the two principal symmetry directions of the ideal hcp lattice, expressed in units of  $[Z^*e^2/M\Omega_0]$ . The notation for the dynamical matrix is the same as in Ref. 12, except that the indices have been put on the same line. The contribution from the nonresponsive compensating background has been included in the diagonal terms. Only those components of the dynamical matrix are given which figure in the computation of the dispersion relations for the two symmetry directions. In the case of  $[0001]$ ,  $D_{22}(\mathbf{q},11)$  and  $D_{22}(\mathbf{q},12)$  are not given, since by symmetry they are identically equal to  $D_{11}(\mathbf{q},11)$  and  $D_{11}(\mathbf{q},12)$ , respectively.

$(q/q_{\max})$	$D_{11}(\mathbf{q},11)$	$D_{33}(\mathbf{q},11)$	$D_{11}(\mathbf{q},12)$	$D_{33}(\mathbf{q},12)$
[0001]				
0.1	0.575	23.988	-0.560	1.119
0.2	0.575	23.988	-0.539	1.078
0.3	0.575	23.988	-0.505	1.010
0.4	0.575	23.988	-0.459	0.917
0.5	0.575	23.988	-0.401	0.801
0.6	0.575	23.988	-0.333	0.666
0.7	0.575	23.988	-0.257	0.514
0.8	0.575	23.988	-0.175	0.350
0.9	0.575	23.988	-0.089	0.177
1.0	0.575	23.988	0.0	0.0

$(q/q_{\max})$	$D_{11}(\mathbf{q},11)$	$D_{22}(\mathbf{q},11)$	$D_{33}(\mathbf{q},11)$	$D_{11}(\mathbf{q},12)$		$D_{22}(\mathbf{q},12)$		$D_{33}(\mathbf{q},12)$	
				Real	Imag.	Real	Imag.	Real	Imag.
[0110]									
0.1	0.624	13.263	11.248	-0.572	0.179	11.810	-0.181	-11.240	0.002
0.2	0.765	13.608	10.762	-0.587	0.356	11.260	-0.372	-10.680	0.016
0.3	0.986	14.125	10.024	-0.610	0.527	10.410	-0.581	-9.802	0.055
0.4	1.264	14.742	9.128	-0.639	0.689	9.338	-0.820	-8.700	0.131
0.5	1.574	15.383	8.177	-0.670	0.839	8.126	-1.097	-7.456	0.257
0.6	1.886	15.983	7.266	-0.700	0.973	6.849	-1.421	-6.150	0.448
0.7	2.168	16.489	6.477	-0.734	1.085	5.564	-1.801	-4.841	0.716
0.8	2.392	16.870	5.871	-0.739	1.172	4.309	-2.249	-3.571	0.077
0.9	2.536	17.104	5.492	-0.741	1.231	3.103	-2.772	-2.363	1.541
1.0	2.586	17.183	5.363	-0.727	1.259	1.950	-3.378	-1.224	2.119

putation in a CDC-3600 computer. In the evaluation of the Coulomb coefficients it was found that a value of  $0.561 \text{ \AA}^{-1}$  for  $\eta$  gave good convergence. With this choice for  $\eta$ , it was necessary to sum over only 50 lattice points in reciprocal space, and up to 30 in real space. The coefficients thus obtained are tabulated in Table I for the principal symmetry directions of the hcp lattice, namely,  $[0001]$  and  $[0110]$ . A check on the coefficients is provided by the conditions<sup>16</sup>

$$\sum_{\alpha} D_{\alpha\alpha}^c(\mathbf{q},kk) = \frac{4\pi(Z^*e^2)^2}{M\Omega_0}; \quad \sum_{\alpha} D_{\alpha\alpha}^c(\mathbf{q},kk') = 0.$$

The values quoted satisfy these relations to within about 0.01%.

It is interesting to compute the phonon frequencies for the case in which the conduction-electron gas is nonresponsive, i.e., does not produce any screening effect. This can be readily done by substituting the Coulomb coefficients for the elements of the dynamical matrix. The frequencies obtained in this way are tabulated in Table II<sup>20</sup> along with the experimental frequencies, all frequencies being expressed in units of  $\nu_p$ , the plasma frequency, which is given by

$$\nu_p = \frac{1}{2\pi} \left( \frac{4\pi(Ze)^2}{M\Omega_0} \right)^{1/2}.$$

From the table it is clear that the electron gas produces large screening effects for the longitudinal

branches. In particular, the percentage screening of the longitudinal acoustic (LA) branch along  $[0001]$  is as large as in lead.<sup>11</sup> The transverse branches are less affected.

Let us now turn our attention to the case where screening effects are taken into account. For this case, the Coulomb contribution was computed with a value of 2.17 for  $Z^*$  as quoted by Harrison.<sup>9</sup> The electronic contribution was determined by carrying out the summations in Eqs. (13) and (14). For  $E(q)$ , we used the

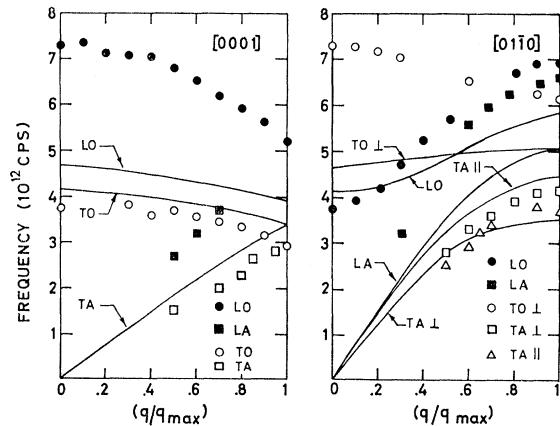


FIG. 1. Phonon dispersion relations in magnesium along the two principal symmetry directions. The solid lines are theoretical curves based on Harrison's pseudopotential results computed from first principles, while the data are those of Iyengar *et al.* The theoretical results for the LA branch along the  $[0001]$  direction are not shown. The frequencies for this branch were found to be imaginary for  $q/q_{\max} < 0.5$ .

<sup>20</sup> In these calculations,  $Z^*$  was set equal to the valency  $Z$ .

TABLE II. Comparison of experimentally measured frequencies for magnesium with those calculated without taking screening into account. All frequencies are expressed in terms of the plasma frequency  $\nu_p = 1.77 \times 10^{13}$  cps. The experimental frequencies were obtained by drawing smooth curves through the datum points of Iyengar *et al.* (Ref. 12).

$(q/q_{\max})$ [0001]	LO		LA		TO		TA	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
0.2	0.403	1.000	0.065	0.963	0.212	0.212	0.034	0.035
0.4	0.397	1.000	0.127	0.966	0.203	0.204	0.068	0.067
0.6	0.371	0.999	0.181	0.972	0.202	0.200	0.102	0.098
0.8	0.335	0.998	0.240	0.978	0.189	0.174	0.129	0.126
1.0	0.294	0.985	0.294	0.985	0.166	0.152	0.166	0.152

$(q/q_{\max})$ [0110]	LO		LA		TO <sub>I</sub>		TA <sub>I</sub>		TA <sub>II</sub>	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
0.2	0.237	1.00	0.119	0.308	0.406	0.932	0.062	0.050	0.062	0.050
0.4	0.297	0.989	0.226	0.467	0.393	0.850	0.124	0.130	0.119	0.114
0.6	0.345	0.965	0.315	0.604	0.368	0.738	0.186	0.212	0.167	0.167
0.8	0.378	0.939	0.356	0.698	0.359	0.624	0.220	0.295	0.206	0.202
1.0	0.389	0.925	0.373	0.734	0.346	0.563	0.235	0.343	0.210	0.215

tabulation provided by Harrison<sup>9,21</sup> with a suitable interpolation formula, and the summation was carried up to  $q = 2\pi\sqrt{14}/a$  ( $a = 3.2028$  Å for Mg), corresponding to about 300 reciprocal lattice points. The two contributions to the dynamical matrix having been determined, it was then diagonalized in the usual way—taking, of course, due advantage of the simplifications provided by symmetry.<sup>12</sup> The theoretical results thus obtained for the [0001] and [0110] directions are compared with the experimental data of Iyengar *et al.*, in Fig. 1.<sup>22</sup> The agreement between theory and experiment is rather poor. Further, according to theory, the frequencies of the LA branch along [0001] are imaginary for  $(q/q_{\max}) < 0.5$ , i.e., the crystal is unstable against these modes of motion—a conclusion contrary to experiment. Theory also predicts incorrectly the order of the two transverse acoustic branches along [0110]. According to theory, the frequencies of the TA<sub>II</sub> branch are higher than those of TA<sub>I</sub> branch, while the reverse is found to be the case experimentally.

In view of the poor performance of the basic  $E(q)$  in predicting phonon frequencies, it was felt desirable to derive  $E(q)$  from experiment using some model. The  $E(q)$  thus obtained should be of value in computing various other properties of the metal.

One possible form for  $E(q)$  is that based on the “Bardeen model”.<sup>23</sup> In this model, the pseudopotential

<sup>21</sup> This  $E(q)$  computed from first principles will hereafter be referred to as basic  $E(q)$  as opposed to a model  $E(q)$ , to be introduced later.

<sup>22</sup> Recently, Squires [in Symposium on Inelastic Scattering of Neutrons by Condensed Systems, Brookhaven National Laboratory, New York, 1965, p. 78 (unpublished)] has remeasured the phonon dispersion relations in magnesium in the basal plane. His results for the [0110] direction are in good agreement with those of Iyengar *et al.* (Ref. 12). In Fig. 1 we show only the data of the latter authors, since a tabulation of their results was readily available.

<sup>23</sup> L. J. Sham and J. Ziman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 221.

is local and has the form<sup>24</sup>

$$v_{pp}(q) = \frac{1}{\Omega_0} \left[ -\frac{4\pi Ze^2}{q^2} + \alpha \right] g(qr_s),$$

where  $r_s$  is the radius of the Wigner-Seitz sphere,

$$g(x) = 3(\sin x - x \cos x)/x^3,$$

and  $\alpha$  is a constant which can be calculated from first principles. In practice,  $\alpha$  is treated as a parameter. The expression for  $E(q)$  in the Bardeen model is

$$E(q) = -\frac{q^2}{8\pi Ze^2 \Omega_0} \left[ \left( -\frac{4\pi Ze^2}{q^2} + \alpha \right) g(qr_s) \right]^2 \times \left( 1 - \frac{1}{\epsilon(q)} \right). \quad (17)$$

$\epsilon(q)$  is the Hartree-self-consistent dielectric function for a free-electron gas, and is given by<sup>19</sup>

$$\epsilon(q) = 1 + \frac{6\pi Ze^2}{q^2 \Omega_0 E_F} \left\{ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right\}.$$

In this expression,  $E_F$  and  $k_F$  are, respectively, the energy and wave number of an electron at the Fermi surface.

Another possible form for  $E(q)$  is that suggested by Harrison,<sup>10</sup> i.e.,

$$E(q) = -\frac{q^2}{8\pi Ze^2 \Omega_0} \left[ -\frac{4\pi Ze^2}{q^2} + \frac{\beta}{[1 + (qr_c)^2]^2} \right]^2 \times \left( 1 - \frac{1}{\epsilon(q)} \right), \quad (18)$$

<sup>24</sup> A. Sjolander, Brookhaven National Laboratory Report No. BNL 940 (C-45), p. 29 (unpublished).

which is based on the local pseudopotential

$$v_{pp}(q) = \frac{1}{\Omega_0} \left[ -\frac{4\pi Z e^2}{q^2} + \frac{\beta}{[1 + (qr_c)^2]^2} \right].$$

Here  $\beta$  and  $r_c$  are parameters to be derived from experiment. Harrison has tried out such a model  $E(q)$  for aluminium and lead and has shown that the model pseudopotential considered should be a reasonably good one for metals having small spin-orbit interaction. Since spin-orbit effects are small in magnesium,<sup>25</sup> we might expect the model  $E(q)$  to be useful for this metal.

Before making calculations using the model  $E(q)$ , it is necessary to first determine the parameters  $\beta$  and  $r_c$ . To do this, we adopted the following procedure, which is similar to that employed earlier by Harrison. Frequencies for two select phonons were calculated for a range of values of  $r_c$ , varying  $\beta$  over a wide range for each  $r_c$ . A preliminary scan of this type showed that values of  $r_c < 0.17$  a.u. were unsuitable, since  $E(q)$  had a very long and large tail. Similarly, values greater than 0.43 a.u. were also unsatisfactory, since  $\beta$  became imaginary.

Having set limits on  $r_c$  by this trial run, the region 0.17–0.43 was then scanned in greater detail until a pair of values for  $r_c$  and  $\beta$  were found which predicted frequencies close to the observed values for the two phonons under consideration. Actually, there were two values of  $\beta$ , both of which could reproduce very nearly the observed frequencies at the two select points in reciprocal space. Of these two values, only one gave an  $E(q)$  similar to the basic  $E(q)$ , and this value of  $\beta$  was preferred for further calculations. The values of the parameters finally chosen by us were  $r_c = 0.265$  a.u. and  $\beta = 37.2$  Ry (a.u.)<sup>3</sup>. This value of  $\beta$  is to be compared with the value of 41.6 derived earlier by Harrison<sup>26</sup> from a consideration of electron scattering on the Fermi surface.

Figure 2 shows the  $E(q)$  according to Eq. (18) with the values quoted above for the two parameters. Also

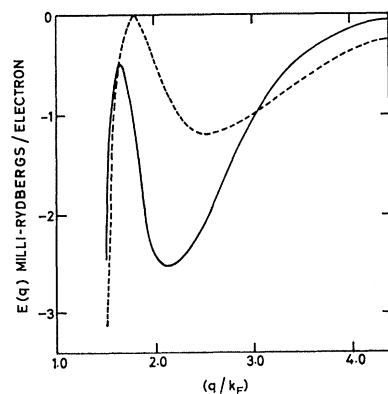


FIG. 2.  $E(q)$  for magnesium as computed by Harrison from first principles (solid curve), and as derived from experimental phonon-dispersion data using a two-parameter model (dashed curve).

<sup>25</sup> L. M. Falicov, Phil. Trans. Roy. Soc. (London) A255, 55 (1962).

<sup>26</sup> W. A. Harrison, Phys. Rev. 131, 2433 (1963).

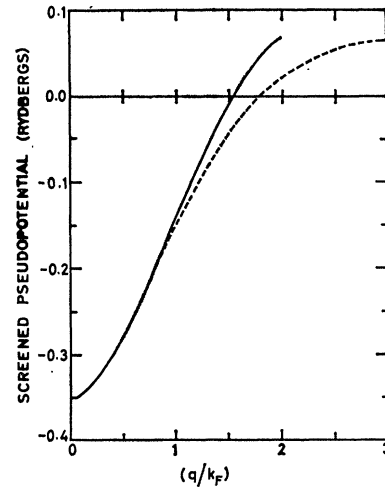


FIG. 3. Screened pseudopotential for magnesium. The solid curve was obtained by Harrison in his basic calculations by considering scatterings restricted to the Fermi surface. This is also referred to as the OPW form factor. The dashed curve is based on the model pseudopotential discussed in the text. The parameters of the model were derived by fitting to two selected measured phonon frequencies.

shown in this figure is the basic  $E(q)$  of Harrison. For values of  $q < k_F$ , the two  $E(q)$ 's agree with each other. In the region beyond  $k_F$ , however, there are significant differences, with the model  $E(q)$  having a longer tail.

We have also computed the screened pseudopotential

$$\left[ -\frac{4\pi Z e^2}{q^2} + \frac{\beta}{[1 + (qr_c)^2]^2} \right] / \Omega_0 \epsilon(q), \quad (19)$$

or what Harrison calls  $\langle \mathbf{k} + \mathbf{q} | \omega | \mathbf{k} \rangle$ . This is shown as a dashed line in Fig. 3 and is compared with the values obtained by Harrison in his basic calculations for the special case where both  $\mathbf{k}$  and  $\mathbf{k} + \mathbf{q}$  lie on the Fermi surface. Once again we find that for  $q < k_F$  the agreement between the basic and model results is good. The differences are in the region  $q > k_F$ .

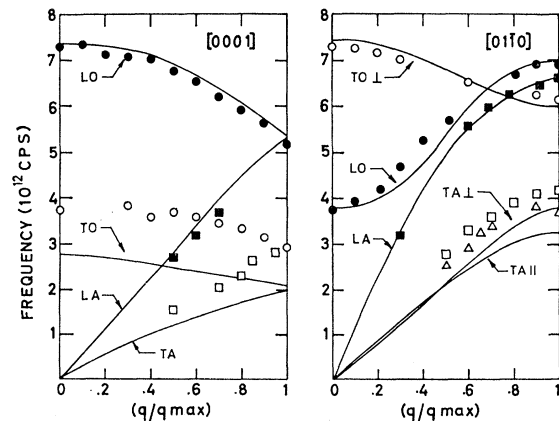


FIG. 4. Comparison of experimentally measured phonon dispersion relations with those theoretically computed using the model pseudopotential. The various symbols have the same meanings as in Fig. 1.

The results for the dispersion relations using the model  $E(q)$  are summarized in Fig. 4. Nearly 900 reciprocal lattice points were included in the summations in Eqs. (13) and (14). Even so, the sums have not converged completely, as evidenced by the small splittings at the zone boundary in the [0001] direction. Comparing Figs. 1 and 4, it is clear that the model pseudopotential has generally been more successful in reproducing the observed frequencies than that computed from first principles. There are, however, important deviations as far as the transverse branches are concerned.

To summarize, phonon frequencies in magnesium computed using pseudopotential results obtained from first principles show poor agreement with experiment. A model pseudopotential involving two parameters has

proved more successful in this respect. Comparison of the pseudopotentials and  $E(q)$  for the two cases shows a difference in the region beyond  $k_F$ . This suggests that better agreement with experiment could be obtained if the accuracy of the basic  $E(q)$  were improved by computing the core energies and orbitals more carefully. We hope to examine this question shortly.

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## Some Analytic Properties of Finite-Band Models in Solids

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The work of Kohn is generalized to more than one dimension for a finite-band model by a simple algebraic procedure. Some results not previously derived for more than one dimension are obtained. The differences between the analytic properties of the model and those of the complete Hamiltonian are briefly discussed.

### INTRODUCTION

IT is well known that the motion of an electron in a crystal is governed in the one-electron approximation by a Hamiltonian which is periodic in the lattice. From this it follows that the wave functions must have the form

$$\phi_n(\mathbf{r}, \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} U_n(\mathbf{r}, \mathbf{k}),$$

where  $U_n$  has the same periodicity in  $\mathbf{r}$  as the Hamiltonian. If the wave functions are to remain finite as  $r \rightarrow \infty$  in any direction, then  $\mathbf{k}$  must have only real components. However, if the crystal has a boundary, i.e., say for  $x > 0$  we have only free space, then we cannot restrict  $k_x$  in the crystal to be real since, if  $k_x$  has a negative imaginary part,  $\phi_n(\mathbf{r}, \mathbf{k})$  will not diverge as  $x \rightarrow -\infty$  and hence is an acceptable solution. Clearly then, these solutions, which are simply the analytic continuation of the Bloch solutions for complex  $\mathbf{k}$ , will have ramifications in problems involving surfaces such as the spectrum of allowed surface states or the matching of electronic wave functions at the boundary of a crystal in a low-energy electron-diffraction experiment. Furthermore, solutions with complex  $\mathbf{k}$  also appear in the theory of electron tunneling and in any physical

problem involving a "tailing off" of the wave function in some classically forbidden region. Finally, we should mention that the rate of decay of Wannier functions is intimately related to the analytic properties of the Bloch waves.

The analytic properties of Bloch waves and Wannier functions have been exhaustively studied by Kohn<sup>1</sup> for the one-dimensional case. However, his methods are based on the theory of ordinary, i.e., not partial differential equations, and cannot be extended to two or three dimensions, not even to a one-dimensional section of a two- or three-dimensional band structure. The latter follows from the fact that in one dimension, bands cannot overlap, whereas in more than one dimension, one-dimensional sections of the energy may overlap. More recently, Blount<sup>2</sup> and Heine<sup>3</sup> have proved some general results concerning the analytic properties of the energy function, but it is not clear how to obtain the analytic properties of the Bloch waves from their work.

All the previously mentioned work makes liberal use of theorems concerning the analytic properties of

<sup>1</sup> W. Kohn, Phys. Rev. **115**, 809 (1959).

<sup>2</sup> E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, pp. 305-373.

<sup>3</sup> V. Heine, Proc. Phys. Soc. (London) **81**, 300 (1963).

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