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Lattice Dynamics of Magnesium from a First-Principles Nonlocal Pseudopotential Approach*

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Harrison's *a priori* theory is used to construct a first-principles nonlocal pseudopotential for magnesium, a metal with the hexagonal close-packed (hcp) structure and two atoms per unit cell. A response function for the exchange interaction among conduction electrons, which uses the Kohn-Sham approximation for the long-wavelength limit, is employed in the calculation of the energy–wave-number characteristic $F(q)$. The phonon spectra were calculated for the [0001], [01$\bar{1}$0], and [11$\bar{2}$0] directions. The theoretical dispersion relations show excellent agreement, for all directions, when compared with data obtained from neutron diffraction experiments. Various other approximations for the inclusion of conduction-electron exchange and correlation are discussed, and the choice of a particular response function is shown to be not significant in these first-principles calculations for hcp metals. Comparison is made with other recent treatments of exchange and correlation effects in different formulations of pseudopotential theory for magnesium. The total binding energy and elastic shear constants are also calculated and show good agreement with experiment.

I. INTRODUCTION

In recent years pseudopotential methods have become very popular as means for calculating phonon spectra, elastic constants, band structures, and other atomic and electronic properties of simple metals (i.e., metals other than noble and transition metals). Until rather recently, the techniques most used involved parametrized model potentials which utilize experimental data directly to adjust the potentials. Furthermore, after the model has been adjusted and made to reproduce the experimental data with sufficient accuracy, it can then be used to calculate additional properties. This approach to the calculation of metallic properties is exemplified by the work of Schneider and Stoll,[1,2] who have successfully applied model potentials to a large number of metals. They have calculated phonon dispersion relations, transport properties, work functions, Fermi surfaces, and other properties of the simple metals. A widely used technique for the construction of model potentials, which combines features of pseudopotential theory and the quantum-defect method, was first suggested by Heine and Abarenkov[3] (HA). In this method, the deep well located at each ion is transformed into a shallow potential, which is usually computed as a function of the angular momentum quantum number. The potential is then adjusted until the logarithmic derivative of the wave function inside some radius matches the logarithmic derivative of the Coulomb wave function outside. This procedure has been optimized by Shaw[4] and used by him and others[5] to calculate metallic properties for a number of the simple metals. We shall refer to this as the optimized Heine-Abarenkov (OHA) method.

It is not too difficult a task to construct a parametrized or fitted model potential which reproduces a single observable property. It is more difficult to construct a model potential from which a number of different properties can be calculated; it is evident that if the number of parameters is increased, almost any conceivable data can be fitted with arbitrary precision. The HA and OHA methods, however, are attempts at limiting the parametrized character of model potential calculations, by incorporating experimental data into the model at a more fundamental level. Because of the quasi-first-principles nature of these methods, the resulting predictions of properties cannot properly be compared with equivalent results from fully fitted models.

A number of authors have attempted to apply the HA and OHA methods to the calculation of phonon dispersion relations and most of these have met with only moderate success. Pindor and Pynn[6] used a local form of the HA method to calculate the phonon spectrum of magnesium, a divalent metal with the hexagonal close-packed (hcp) structure, with rather poor results. A calculation using the OHA method was carried out for magnesium by Gilat, Rizzi, and Cubiotti[5] with only slightly better results. In an attempt to improve the calculation, Gilat *et al.* treated the electron mass as an adjustable parameter. They were able to obtain substantially better agreement with experiment by taking the effective electron mass to be $1.6m_e$. Another recent calculation of the magnesium phonon spectrum with the OHA technique was published by Shaw and Pynn[7] (SP). To include a correction for the conduction-electron exchange in the calculation of the energy-wave-number characteristic $F(q)$, they use both the Kohn-Sham[8] and Slater[9] approximations for the limit $q \to 0$ in the exchange response function. The phonon dispersion relations that SP obtain with the Kohn-Sham potential compare equally as well with experiment as the results Gilat *et al.* obtained using only the free-electron mass. The results that SP obtained with the Slater approximation are in somewhat better agreement with experiment but they view this as fortuitous since they contend that the Kohn-Sham limit is physically more reasonable. The phonon frequencies for magnesium were also calculated by Prakash and Joshi,[10] who used a single-orththogonalized-plane-wave electron-ion matrix element and the Kohn-Sham[8] exchange potential. Their results show rather uneven agreement when compared to experiment. A different procedure was followed by Brovman, Kagan, and Holas,[11] who used the HA model potential and modified it by the introduction of noncentral forces with a four-parameter fitting technique.

Most recently, Floyd and Kleinman[12] computed the phonon spectrum of magnesium with a local model pseudopotential containing two adjustable parameters. These authors, using the Kleinman-Langreth[13,14] dielectric function, are able to obtain a very close fit with the experimental data by selecting the parameters in their model pseudopotential. Furthermore, to investigate the effects of different dielectric response functions on the phonon dispersion relations, they (i) held all parameters fixed, and (ii) replaced, in turn, the Kleinman-Langreth by the Hubbard[15] and RPA dielectric functions and recalculated the spectrum, finding, not unexpectedly, poorer agreement with the latter two response functions. These authors have stated that they used a model pseudopotential because "···there is no way of knowing the 'correc'' pseudopotential (or of calculating with sufficient accuracy a first-principles potential). . . ." Contrary to this assertion, a similar procedure employing a first-principles pseudopotential is more logically able to demonstrate any sensitivity in the calculation of a phonon spectrum to the choice of a dielectric response function.

The present work represents part of a systematic study applying a first-principles nonlocal pseudopotential theory to the calculation of a range of atomic and electronic properties of metals. The theory was suggested by Harrison[16] and based upon the original orthogonalized-plane-wave[17] (OPW) pseudopotential formalism by Phillips and Kleinman.[18] All model potentials, including the HA, the OHA, and the fully parametrized methods, require more experimental input than Harrison's single-OPW formulation of the pseudopotential, which we shall refer to as the Harrison first-principles (HFP) method. In principle, the HFP method requires only the lattice constants, atomic number, and the fundamental constants as input to the theory. One of the first attempts to use the nonlocal HFP theory for divalent metals was carried out by Roy and Venkataraman.[19] Using the $F(q)$ published by Harrison,[20] they calculated phonon dispersion relations for magnesium which compared very poorly with experiment. Even though they made some unfortunate errors in the dynamical matrix, the results were not much improved when the errors were corrected. The first successful HFP calculation for the phonon dispersion relations of an hcp metal was reported by the present authors for beryllium.[21] The pseudopotential used in the $F(q)$ for this calculation was constructed with an analytic wave function for Be^{++} from Green *et al.*[22] In a recent paper[23] (hereafter referred to as I) we adopted a more general approach to the construction of $F(q)$ with Hartree-Fock-Slater (HFS) wave functions.[24] This was used to compute the phonon spectrum and elastic constants for beryllium; again, as in the case with the analytic wave function, good agreement was obtained when compared with experimental results. Preliminary calculations for magnesium[25] indicated that the theoretical phonon dispersion relations would be in even better agreement with experiment than the beryllium results and the subsequent work reported here bears this out.

As a very detailed presentation of first-principles pseudopotential theory is given by Harrison,[26] we shall merely outline the parts of the theory relevant to the present calculations. This is discussed in Sec. II. The problem of conduction-electron exchange and correlation is treated in Secs. II C and also III, where the detailed calculations and a comparison of the results with other recent work are discussed.

II. THEORY

Magnesium has the hcp crystal structure with two atoms per unit cell. The lattice may be described by a unit cell with edges

$$\vec{a}_1 = c\hat{e}_z \quad , \quad \vec{a}_2 = a\hat{e}_x \quad , \quad \vec{a}_3 = -\tfrac{1}{2}a\,\hat{e}_x + \tfrac{1}{2}\sqrt{3}a\,\hat{e}_y \quad ,$$

where a and c are the lattice constants and $\hat{e}_x$, $\hat{e}_y$, and $\hat{e}_z$ are unit orthogonal vectors. One atom is located at the origin while the other atom is at $(\frac{1}{2}, \frac{1}{3}, \frac{2}{3})$, referred to the hexagonal axes, or at

TABLE I. Physical parameters for magnesium in atomic units.

Parameter	Value
a	6.06475
c	9.84627
c/a	1.6235
Atomic mass M	22158
Atomic number A	12
Valence Z	2
Effective valence Z^*	2.1542
Ω_{uc}	313.6378
Ω_0	156.8189
k_f	0.72280
Plasma frequency, units of 10^{13} Hz	1.906

$$\tfrac{1}{3}\sqrt{3}\; a\hat{e}_y + \tfrac{1}{2} c\; \hat{e}_z$$

in the Cartesian system. The volume per unit cell is

$$\Omega_{uc} = \tfrac{1}{2} c\sqrt{3}\; a^2 \quad ,$$

and the atomic volume Ω_0 is defined to be the volume of a unit cell divided by the number of atoms in that cell. We let $\vec{d}_j$ identify the jth atom in the unit cell and $\vec{K}$ be a reciprocal-lattice vector defined such that its components $\vec{K}_j$ satisfy the condition

$$\vec{a}_i \cdot \vec{K}_j + 2\pi\delta_{ij} \quad ,$$

where $\vec{a}_i$ are the primitive lattice vectors. The lattice constants and other relevant parameters are listed in Table I. Unless otherwise noted, all numerical values are given in atomic units such that $\hbar = \frac{1}{2}e^2 = 2m = 1$ and energy is in rydbergs.

A. Pseudopotential

Since Harrison[26] has given an excellent treatment of the general pseudopotential theory used here, there is little need to duplicate his work and we shall restrict ourselves to a brief outline of the results which are relevant to the present calculations. Because of the fundamental approximations upon which it is based, the application of this theory is limited to the simple metals. These are (i) the use of a self-consistent field, (ii) the small-core approximation, and (iii) the use of perturbation theory to compute the conduction-band states. Harrison has recently reformulated this simple-metal pseudopotential and extended it to the transition metals.[27] Since magnesium is a simple divalent metal, however, we will not discuss this more general formulation.

In addition to the Coulomb interaction between the conduction electrons and the ion cores, there are also, as a consequence of the antisymmetrization requirements, exchange interactions between electrons. It can be shown that the conduction-core exchange interaction gives rise to an effective repulsive potential. These attractive and repulsive terms tend to cancel and the small net effective potential is called the pseudopotential. The HFP theory depends upon a transformation of the one-electron Schrödinger equation by an expansion of the true wave functions in single OPW's. When the terms are rearranged, a transformed wave equation or pseudoequation is obtained in which the small effective potential $W(\vec{r})$ is explicitly displayed. In the calculation of this pseudopotential, we assume that the core wave functions are the same as those in the free ion but that the core eigenvalues E_α are not. A further assumption is that the pseudopotential can be written as the sum of spherically symmetric pseudopotentials centered at the ion positions $\vec{r}_j$,

$$W(\vec{r}) = \textstyle\sum_j w(\vec{r} - \vec{r}_j) \quad .$$

This allows the matrix elements of $W(\vec{r})$ to be expressed as

$$\langle \vec{k} + \vec{q} \,|\, W \,|\, \vec{k} \rangle = S(\vec{q})\; \langle \vec{k} + \vec{q} \,|\, w \,|\, \vec{k} \rangle \quad ,$$

where $\vec{k}$ identifies the electron state, $\vec{q}$ is a vector in the reciprocal lattice, and $S(\vec{q}) = N^{-1}\sum_j e^{i\vec{q}\cdot\vec{r}_j}$ is a structure factor, with N the total number of ions. We will also separate $W(\vec{r})$ into the sum of $W^0(\vec{r})$, a part due to the ions, and $W^1(\vec{r})$, a screening part due to the conduction electrons.

After the structure factors are factored out of the pseudopotential matrix elements we have

$$\langle \vec{k} + \vec{q} \,|\, w \,|\, \vec{k} \rangle = \langle \vec{k} + \vec{q} \,|\, w^0 \,|\, \vec{k} \rangle + \langle \vec{k} + \vec{q} \,|\, w^1 \,|\, \vec{k} \rangle \quad .$$

The matrix element for the unscreened component is

$$\langle \vec{k} + \vec{q} \,|\, w^0 \,|\, \vec{k} \rangle = v_q^0 + \langle \vec{k} + \vec{q} \,|\, w^R \,|\, \vec{k} \rangle \quad ,$$

where $\langle \vec{k} + \vec{q} | w^R | \vec{k} \rangle$ is the repulsive term[26] and v_q^0 is the Fourier transform of the crystal potential. An explicit expression for the screening field, which we shall denote by $w_q^1 = \langle \vec{k} + \vec{q} | w^1 | \vec{k} \rangle$, is

$$w_q^1 = v_q^0 [1 - \epsilon^*(q)]/\epsilon^*(q) + v_q^R [1 - G(q)]/\epsilon^*(q) \; ,$$

where

$$v_q^R = \frac{4}{\pi^2 q^2} \int \frac{\langle \vec{k} + \vec{q} | w^R | \vec{k} \rangle}{k^2 - |\vec{k} + \vec{q}|^2}\, d^3k \quad ,$$

and $\epsilon^*(q)$ is a dielectric function modified to include conduction-electron exchange and correlation effects. Selected values of v_q^R are listed in Table II. The function $G(q)$ is the normalized conduction-electron exchange and correlation interaction; an approximation for this function, as well as for $\epsilon^*(q)$, is given in Sec. II C.

The energy of the state $\vec{k}$ is obtained by the usual second-order perturbation theory from the pseudoequation. Then by summing the perturbation expansion over the spherical Fermi surface, the

TABLE II. Selected values of v_q^R. The notation $n\,Em$ means $n \times 10^m$.

q/k_F	$-v_q^R$	q/k_F	$-v_q^R$
0.01	9.8914 E3	2.2	4.7286 E-2
0.1	9.8760 E1	2.4	2.8836 E-2
0.2	2.4573 E1	2.6	1.8452 E-2
0.4	6.0265 E0	2.8	1.2209 E-2
0.6	2.5929 E0	3.0	8.2930 E-2
0.8	1.3911 E0	3.2	5.7561 E-2
1.0	8.3559 E-1	3.4	4.0702 E-2
1.2	5.3438 E-1	3.6	2.9258 E-2
1.4	3.5310 E-1	3.8	2.1345 E-2
1.6	2.3539 E-1	4.0	1.5785 E-2
1.8	1.5366 E-1	5.0	4.1549 E-4
2.0	8.8132 E-2	10.0	7.5993 E-6

total electron energy per ion can be found. Since the Coulomb interaction between any two electrons is counted twice by this method, an energy equal to this interaction must be substracted from the total energy. The second-order term in the total energy is then combined with this electron-electron interaction to form the band-structure energy

$$E_{\mathrm{bs}} = \sum_q{}' |S(\vec{q})|^2 F(q) \quad .$$

In atomic units, $F(q)$ is given by[28]

$$F(q) = \frac{2\Omega_0}{(2\pi)^3} \int \frac{|\langle \vec{k}+\vec{q}\,|w|\,\vec{k}\rangle|^2}{k^2 - |\vec{k}+\vec{q}|^2}\, d^3k - \frac{q^2\Omega_0}{16\pi}\, |w_q^1|^2 \quad .$$

It should be noted that this function, the energy–wave-number characteristic, is dependent upon the atomic volume but is independent of the actual atomic configuration. Some authors (cf. Shaw and Pynn[7]) use a normalized $F(q)$ defined as

$$F_N(q) = -F(q)\,(2\pi e^2 Z^{*2}/q^2\Omega_0)^{-1},$$

where the limit of $F(q)$ as $q \to 0$ is

$$F(q) \to -2\pi e^2 Z^{*2}/q^2\Omega_0$$

and Z^* is the effective valence.

B. Crystal Potential

The prescription for the calculation of the crystal potential for magnesium is similar to that described in I for beryllium, and we shall briefly outline only those contributions to the potential that are computed differently. The interactions that contribute to this potential are (i) potential due to the ion core, (ii) conduction-band–core exchange, (iii) correlation between conduction and core electrons, (iv) potential due to conduction electrons, and (v) screening potential. The exchange and correlation among conduction electrons will be treated separately in Sec. II C. In general, one should also consider additional contributions to the potential such as the correlation among the core electrons, the deviation from spherical symmetry around the core, the spin-orbit coupling, etc. In magnesium,[29] however, it has been shown that these contributions make only minor or negligible changes in the crystal potential and we shall, therefore, not include them. We write the transform of the crystal potential as

$$v_q^0 = v_q^{(1)} + v_q^{(2)} + v_q^{(3)} + v_q^{(4)} \quad ,$$

where the notation is described in the subsequent discussion.

1. *Potential due to Ion Core*

Following Harrison,[30] we decompose the ion-core contribution into two components, one of which is the valence-charge potential given by

$$v_q^{(1v)} = -(4\pi e^2/\Omega_0 q^2)\,Z \quad .$$

The other part, which consists of the remainder of the nuclear charge and the potential due to the core electrons, is given by

$$v_q^{(1c)} = -(4\pi e^2/q^2\Omega_0)\,[A - Z - n(\vec{q})] \quad ,$$

where Z is the valence and A is the atomic number. The transform of $\rho(\vec{r})$, the core-electron density, is given by $n(\vec{q})$ and is defined such that $n(0)$ equals the number of core electrons, viz.,

$$n(\vec{q}) = \int \rho(\vec{r})\, e^{-i\vec{q}\cdot\vec{r}}\, d\vec{r} \quad .$$

This electron density is tabulated in Table III, column 2.

In the evaluation of the expression which includes the core shift, the value of $v_q^{(1c)}$ at $q = 0$ is required. This term is given by

$$v_0^{(1c)} = -\frac{2\pi e^2}{3\Omega_0} \sum_{nl} \int 2(2l+1)\, P_{nl}^2(r)\, r^2\, dr \quad ,$$

where $P_{nl}(r)$ is the radial part of the core wave function and the integration is terminated at the radius of the atomic sphere. The total ion-core contribution is then

$$v_q^{(1)} = v_q^{(1v)} + v_q^{(1c)} \quad .$$

This contribution is tabulated in Table III, column 3, for selected values of q/k_F.

2. *Conduction-Band–Core Exchange*

We used the Kohn-Sham[8] effective exchange potential to calculate the conduction-band–core exchange contribution to the crystal potential. Kohn and Sham essentially evaluated the energy-dependent exchange potential at the Fermi surface, rather than averaging over all occupied state in the Fermi sphere as in the Slater approximation. This results in an effective potential that is two-thirds of the Slater approximation,

$$v_q^{(2)} = (4\pi/\Omega_0 q) \int v^{(2)}(r)\, r \sin qr\, dr,$$

TABLE III. Fourier components of the potential contributions used in the calculation of the pseudopotential matrix elements.

q/k_F	$n(q)$	$-v_q^{(1)}$	$-v_q^{(2)}$	$-v_q^{(3)}$	$-v_q^{(4)}$
0.00	10.0000	· · ·	0.2185	0.0032	· · ·
0.01	9.9999	6135.3888	0.2350	0.0032	473.0584
0.05	9.9991	245.5284	0.2348	0.0032	18.9206
0.10	9.9962	61.4702	0.2342	0.0032	4.7288
0.20	9.9847	15.4556	0.2318	0.0032	1.1808
0.30	9.9656	6.9342	0.2280	0.0031	0.5238
0.40	9.9390	3.9515	0.2227	0.0031	0.2939
0.50	9.9050	2.5708	0.2162	0.0031	0.1874
0.60	9.8636	1.8205	0.2085	0.0030	0.1296
0.70	9.8150	1.3679	0.1999	0.0030	0.0948
0.80	9.7595	1.0739	0.1906	0.0029	0.0721
0.90	9.6971	0.8722	0.1807	0.0029	0.0566
1.00	9.6282	0.7276	0.1704	0.0028	0.0456
1.10	9.5529	0.6204	0.1600	0.0027	0.0374
1.20	9.4715	0.5387	0.1496	0.0026	0.0311
1.30	9.3843	0.4748	0.1393	0.0025	0.0263
1.40	9.2915	0.4239	0.1293	0.0025	0.0224
1.50	9.1935	0.3826	0.1197	0.0024	0.0193
1.60	9.0905	0.3486	0.1106	0.0023	0.0168
1.70	8.9829	0.3203	0.1020	0.0022	0.0147
1.80	8.8710	0.2963	0.0940	0.0021	0.0130
1.90	8.7551	0.2757	0.0865	0.0020	0.0115
2.00	8.6356	0.2580	0.0796	0.0019	0.0102
2.10	8.5127	0.2426	0.0732	0.0018	0.0091
2.20	8.3869	0.2290	0.0673	0.0017	0.0082
2.30	8.2583	0.2170	0.0619	0.0016	0.0074
2.40	8.1275	0.2062	0.0570	0.0015	0.0067
2.50	7.9946	0.1966	0.0524	0.0014	0.0061
2.60	7.8600	0.1879	0.0482	0.0013	0.0055
2.80	7.5869	0.1727	0.0408	0.0011	0.0046
3.00	7.3105	0.1598	0.0345	0.0009	0.0038
3.20	7.0330	0.1488	0.0292	0.0008	0.0033
3.40	6.7563	0.1392	0.0247	0.0006	0.0028
3.60	6.4823	0.1306	0.0209	0.0005	0.0024
4.00	5.9480	0.1160	0.0153	0.0003	0.0018
4.50	5.3184	0.1012	0.0106	0.0001	0.0012
5.00	4.7430	0.0891	0.0073	0.0000	0.0009
6.00	3.7758	0.0701	0.0038	· · ·	0.0005
7.00	3.0473	0.0561	0.0021	· · ·	0.0003
8.00	2.5203	0.0454	0.0014	· · ·	0.0002
9.00	2.1477	0.0373	0.0009	· · ·	0.0001
10.00	1.8732	0.0310	0.0007	· · ·	0.0001

where

$$v^{(2)}(\vec{r}) = -(e^2/\pi)[3\pi^2\rho(\vec{r})]^{1/3} .$$

Values of this potential are listed in column 4 of Table III. The contributions 3–5 are discussed in I and the transforms $v_q^{(3)}$ and $v_q^{(4)}$ are listed in Table III, columns 5 and 6, respectively.

C. Exchange and Correlation among Conduction Electrons

These interactions can be included in the calculation by assuming their effect is to modify the screening potential W_q^1. This results in the following matrix element of the total screening potential seen by an electron[30]:

$$W_q^1 = (4\pi e^2/q^2 + X_q)n_q ,$$

where n_q is the conduction-electron density and X_q is the exchange and correlation interaction. When the pseudopotential is formulated with this screening potential, the dielectric function that obtains is

$$\epsilon^*(q) = 1 + [1 - G(q)][\epsilon(q) - 1] \ , \qquad (1)$$

where $G(q)$ is the exchange and correlation interaction normalized to the Coulomb interaction,

$$G(q) = -q^2 X_q / 4\pi e^2 \ .$$

The Hartree dielectric function $\epsilon(q)$ is given by[31]

$$\epsilon(q) = 1 - (4\pi e^2/q^2)\chi(q) \ ,$$

where $\chi(q)$, the free-electron susceptibility at the zero-frequency limit, is

$$\chi(q) = -\frac{n}{\frac{2}{3}E_F}\left[\frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q}\ln\left(\frac{2k_F + q}{2k_F - q}\right)\right] ,$$

where n is the total density of electrons per unit volume, and E_F is the Fermi energy.

Since there is as yet no exact analysis for the response of an electron gas at metallic densities to a perturbation with intermediate wavelength, a usual method of obtaining an expression for the interaction involves postulating a formula that interpolates between the long- and short-wavelength limits, where the response functions are known more accurately. In the present calculations, we have found the correlation contribution to be very small, when compared to the exchange interaction, and we have therefore neglected it. At very short wavelengths, we use Hubbard's[32,15] result that the exchange interaction among parallel spin electrons effectively cancels half of the direct (i.e., Coulomb) interaction. This leads to

$$X_q \to -2\pi e^2/q^2 \ ,$$

as q becomes large. At long wavelengths, as q goes to zero, X_q should approach the exchange potential for a uniform electron gas at the appropriate density. For this limit we have used the Kohn-Sham[8] effective exchange potential, which results in

$$X_0 = -e^2\pi/k_F^2 \ ,$$

where k_F is the Fermi wave vector. A formula that will interpolate between these limits is[21]

$$G(q) = \tfrac{1}{2}[q^2/(q^2 + 2k_F^2)] \ . \qquad (2)$$

There is some question as to whether Hubbard's limit for large q is exact or even correct. Heine and Weaire[33] suggest that the ratio of the exchange to the direct interaction may, more appropriately, be between $\frac{1}{2}$ and 1. However, as our previous results have indicated that the inclusion of the conduction-electron exchange makes only a small correction in the calculated properties[34,23] the precise numerical value of the ratio is of limited significance here. Interpolation formulas used by other authors differ only slightly from Eq. (2). In the same notation as Eq. (2), expressions used by others are Hubbard[15]: $\frac{1}{2}[q^2/(q^2+k_F^2)]$; Sham[35]: $\frac{1}{2}[q^2/(q^2+k_F^2+k_s^2)]$; Shaw and Pynn[7]: $\frac{1}{2}[1 - e^{-q^2/\beta k_F^2}]$, where $\beta = 2$ for the Kohn-Sham approximation and $k_s \approx 4k_F/\pi$. The modified dielectric functions that result when any of these interpolation formulas are used in Eq. (1) do not differ greatly from one another, as can be seen in Fig. 1. Our results thus agree with those of Moriarty,[36] who concludes that the conduction-electron exchange has only a minimal effect on the energy–wave-number characteristic. This point is considered further in Sec. III. In Table IV, we have listed values of $\epsilon^*(q)$, obtained when the interpolation formula (2) is used in the response function; the Hartree dielectric function is also included in Table IV for comparison with $\epsilon^*(q)$.

D. Core Shift

In the HFP theory, one assumes that the wave functions for the ion remain rigid in the metal but that the core eigenvalues are shifted from their values in the free ions. This shift in energy is called[30] the orthogonalization hole potential v_{OPW}. For the core wave functions in the metal, we have used the HFS wave functions[24] for the free ions. For this choice, the zeroth-order approximations to the E_α, the core eigenvalues, are just the HFS eigenvalues ϵ_{nl}. However, this is found to be too crude an approximation and we have instead calculated v_{OPW} and its average value v^*_{OPW} by the method described in I.

In the calculation of the matrix elements necessary to the construction of $F(q)$, the core eigen-

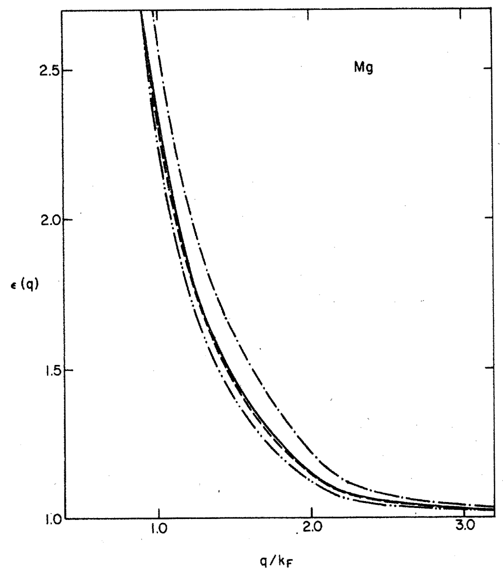

FIG. 1. Different dielectric functions modified to include conduction-electron exchange: Hartree (dash-dot), Shaw and Pynn (Ref. 7) (dash-dot-dot), Sham (Ref. 35) (small dash), King and Cutler (solid).

TABLE IV. The Hartree and modified dielectric at selected values of q/k_F.

q/k_F	$\epsilon(q)$	$\epsilon^*(q)$	q/k_F	$\epsilon(q)$	$\epsilon^*(q)$
0.01	17 616.3	17 615.8	2.2	1.1291	1.0834
0.1	177.0072	176.5693	2.4	1.0857	1.0539
0.2	44.8914	44.4611	2.6	1.0599	1.0368
0.4	11.8616	11.4594	2.8	1.0433	1.0261
0.6	5.7436	5.3818	3.0	1.0322	1.0190
0.8	3.6006	3.2853	3.2	1.0245	1.0143
1.0	2.6065	2.3387	3.4	1.0190	1.0109
1.2	2.0639	1.8412	3.6	1.0150	1.0085
1.4	1.7333	1.5518	3.8	1.0120	1.0067
1.6	1.5141	1.3698	4.0	1.0097	1.0054
1.8	1.3563	1.2462	5.0	1.0039	1.0021
2.0	1.2202	1.1468	10.0	1.0002	1.0001

values always appear together with the diagonal elements of the crystal potential as

$$V_\alpha = \langle \vec{k} | V | \vec{k} \rangle - E_\alpha \ , \qquad (3)$$

where the subscript α refers to the quantum numbers n and l. The contributions to V_α due to $v_0^{(1c)}$, $v_0^{(2)}$, and $v_0^{(3)}$ are easily obtained from the expressions in Sec. II B. For $v_0^{(1v)}$ and $v_0^{(4)}$ we use an approximation described by Harrison,[30]

$$v_0^{(1v)} + v_0^{(4)} \approx -(\tfrac{9}{5}) Z^* e^2 / r_0 \ ,$$

where r_0 is the radius of the atomic sphere. Equation (3) is then explicitly given by

$$V_{nl} \approx -\tfrac{9}{5} Z^* e^2 / r_0 + v_0^{(1c)} + v_0^{(2)} + v_0^{(3)} - \epsilon_{nl} - v_{\text{OPW}} \ .$$

These results are listed in Table V.

E. Lattice Dynamics

In the framework of the Born–von Kārmān theory of lattice dynamics,[37] the phonon frequencies are given by the solution to

$$\det[D_{\alpha\beta}(\vec{Q}, jj') - \omega^2 M \delta_{jj'} \delta_{\alpha\beta}] = 0 \ ,$$

where $D_{\alpha\beta}(\vec{Q}, jj')$ represents a general element of the dynamical matrix, M is the ionic mass, and $\vec{Q}$ is the wave vector of the disturbance. Generally, the dynamical matrix is composed of three parts:

$$D_{\alpha\beta} = D_{\alpha\beta}^C + D_{\alpha\beta}^E + D_{\alpha\beta}^R \ .$$

The $D_{\alpha\beta}^R$ is the ion-ion repulsive contribution, caused by the exchange overlap between ion cores. Since the small cores in magnesium have little overlap, we will assume that this term is very small and neglect it in our calculations. The Coulombic or Ewald contribution $D_{\alpha\beta}^C$ is due to the electrostatic interaction between the ions while $D_{\alpha\beta}^E$, the electronic or band-structure contribution, arises from the electron-ion-electron interaction. The Coulombic term can be computed with methods due to Ewald[38] and Thompson[39] for a lattice of point ions immersed in a uniform compensating background of negative charge. A very clear derivation of this contribution has been given by Cochran.[40] Although the analysis is rather tedious, the results can be stated succinctly if we define the following terms:

$$T_{\alpha\beta}^{(1)}(\vec{a}, jj') = \frac{(\vec{a} + \vec{d}_{j'} - \vec{d}_j)_\alpha (\vec{a} + \vec{d}_{j'} - \vec{d}_j)_\beta}{|\vec{a} + \vec{d}_{j'} - \vec{d}_j|^2} \ ,$$

$$T_{\alpha\beta}^{(2)}(\vec{a}, jj') = \frac{3 \operatorname{erfc}(\eta |\vec{a} + \vec{d}_{j'} - \vec{d}_j|)}{|\vec{a} + \vec{d}_{j'} - \vec{d}_j|^3} + \frac{6\eta}{\sqrt{\pi}} \frac{e^{-\eta^2 |\vec{a} + \vec{d}_{j'} - \vec{d}_j|^2}}{|\vec{a} + \vec{d}_{j'} - \vec{d}_j|^2}$$

$$+ \frac{4\eta^3}{\sqrt{\pi}} e^{-\eta^2 |\vec{a} + \vec{d}_{j'} - \vec{d}_j|^2} \ ,$$

$$T_{\alpha\beta}^{(3)}(\vec{a}, jj') = \frac{\operatorname{erfc}(\eta |\vec{a} + \vec{d}_{j'} - \vec{d}_j|)}{|\vec{a} + \vec{d}_{j'} - \vec{d}_j|^3} + \frac{2\eta}{\sqrt{\pi}} \frac{e^{-\eta^2 |\vec{a} + \vec{d}_{j'} - \vec{d}_j|^2}}{|\vec{a} + \vec{d}_{j'} - \vec{d}_j|^2} \ ,$$

$$A_{\alpha\beta}(\vec{Q}, jj') = \frac{4\pi}{s\Omega_0} \sum_{\vec{K}} \frac{(\vec{K} + \vec{Q})_\alpha (\vec{K} + \vec{Q})_\beta}{|\vec{K} + \vec{Q}|^2}$$

$$\times e^{-|\vec{K} + \vec{Q}|^2 / 4\eta^2} e^{i\vec{K} \cdot (\vec{d}_j - \vec{d}_{j'})} \ ,$$

and

$$B_{\alpha\beta}(\vec{Q}, jj') = \sum_{\vec{a}}{}' \{ T_{\alpha\beta}^{(1)}(\vec{a}, jj') T_{\alpha\beta}^{(2)}(\vec{a}, jj')$$

$$- T_{\alpha\beta}^{(3)}(\vec{a}, jj') \delta_{\alpha\beta} \} e^{i\vec{Q} \cdot (\vec{a} + \vec{d}_{j'} - \vec{d}_j)} \ ,$$

where $\operatorname{erfc}(x)$ is the complementary error function, s is the number of atoms in a unit cell, Ω_0 is the atomic volume, and primes over sums mean the denominators are never zero. The parameter η is chosen to make both the sums in direct and reciprocal space converge rapidly. We have found

TABLE V. Components used the the calculation of V_{nl}. All values are in atomic units with energy in rydbergs.

Component	Values
$v_0^{(1c)}$	−0.117 51
$v_0^{(2)}$	−0.218 48
$v_0^{(3)}$	−0.003 18
v_{OPW}^*	−0.754 17
$(-\frac{9}{5}) Z^* e^2 / r_0$	2.318 22
r_0	3.345 31
ϵ_{10}	−96.484 37
ϵ_{20}	−8.047 96
ϵ_{21}	−5.636 41
V_{10}	94.581 15
V_{20}	6.144 47
V_{21}	3.733 19

that $\eta = (4/\Omega_0)^{1/3}$ usually gives good results. With these definitions, the dynamical matrix can be written

$$D^C_{\alpha\beta}(\vec{Q}, jj') = Z_j^2\{A_{\alpha\beta}(\vec{Q}, jj') - B_{\alpha\beta}(\vec{Q}, jj') + \sum_{j''}{}'[B_{\alpha\beta}(0, jj'') - A_{\alpha\beta}(0jj'')]\delta_{jj'}\} ,$$

where Z_j is the charge on the jth ion.

The band-structure or electronic contribution can be derived by introducing a periodic disturbance of wave vector $\vec{Q}$ into the expression for E_{bs} and expanding the structure factors to secord order in the amplitudes of the disturbance. When the equilibrium band-structure energy is subtracted we obtain

$$D^E_{\alpha\beta}(\vec{Q}, jj') = \sum_{\vec{K}}\{(\vec{K}+\vec{Q})_\alpha(\vec{K}+\vec{Q})_\beta F(|\vec{K}+\vec{Q}|) \times e^{i\vec{K}\cdot(\vec{d}_j-\vec{d}_{j'})} - K_\alpha K_\beta \xi(j) F(K)\delta_{jj'}\} ,$$

where $\xi(j) = \sum_{j'} \cos[\vec{K}\cdot(\vec{d}_j - \vec{d}_{j'})]$. When $K=0$, the term involving $F(K)$ is omitted. This derivation is discussed in some detail by Harrison.[41]

F. Total Energy

For our purposes, it is convenient to separate the total energy into two parts: (i) the free-electron energy which is a function of the volume but not of the specific ionic coordinates, and (ii) the configuration-dependent part which consists of the electrostatic energy, the repulsive energy, and the electronic energy.

The volume-dependent free-electron energy per ion is obtained from the zeroth- and first-order terms in the perturbation expansion of the electron energy. Harrison[30] has derived an explicit expression for this energy, which is given in atomic units by

$$E_{fe} = \tfrac{3}{5}Zk_F^2 + Z^*(v_0^{(1c)} + v_0^{(2)}) - \tfrac{1}{2}v^*_{0PW}(Z^* - Z) + N^{-1}\sum_{\vec{k}}\sum_{nl}(k^2 + |\epsilon_{nl}|)\frac{\langle\vec{k}|nl\rangle\langle nl|\vec{k}\rangle}{1-\langle\vec{k}|p|\vec{k}\rangle} + ZE_{xc} .$$

The p is a projection operator which projects functions onto the core states,

$$p = \sum_{nl} |nl\rangle\langle nl| ,$$

and E_{xc} is the conduction-electron exchange and correlation energy. We used the Gell-Mann and Brueckner[42] expression to approximate this energy:

$$E_{xc} = -0.916/r_s + 0.0622 \ln r_s - 0.096 \text{ Ry} ,$$

where $r_s = (3/4\pi n)^{1/3}$ and n is the electron density.

The electrostatic energy is due to the Coulomb interaction between ions. It can be calculated by

TABLE VI. Energy-wave number characteristic for magnesium, including a correction for conduction-electron exchange, in units of rydbergs per electron. The notation nEm means $n\times10^m$.

q/k_F	$F(q)/Z$	q/k_F	$F(q)/Z$
0.01	−3.558 485 E3	2.10	−1.789 608 E-3
0.03	−3.950 078 E2	2.20	−1.821 337 E-3
0.05	−1.419 299 E2	2.30	−1.778 989 E-3
0.07	−7.220 479 E1	2.40	−1.680 576 E-3
0.09	−4.351 184 E1	2.50	−1.546 259 E-3
0.10	−3.516 418 E1	2.60	−1.393 109 E-3
0.20	−8.478 756 E0	2.70	−1.234 003 E-3
0.30	−3.546 280 E0	2.80	−1.077 898 E-3
0.40	−1.830 377 E0	2.90	−9.305 490 E-4
0.50	−1.046 917 E0	3.00	−7.952 757 E-4
0.60	−6.318 133 E-1	3.10	−6.736 548 E-4
0.70	−3.913 311 E-1	3.20	−5.660 762 E-4
0.80	−2.441 861 E-1	3.30	−4.721 647 E-4
0.90	−1.512 562 E-1	3.40	−3.910 866 E-4
1.00	−9.172 143 E-2	3.50	−3.217 602 E-4
1.10	−5.361 126 E-2	3.60	−2.629 971 E-4
1.20	−2.960 577 E-2	3.80	−1.723 841 E-4
1.30	−1.499 816 E-2	4.00	−1.102 548 E-4
1.40	−6.636 166 E-3	4.50	−3.289 481 E-5
1.50	−2.351 341 E-3	5.00	−9.219 539 E-6
1.60	−6.166 986 E-4	5.50	−3.047 202 E-6
1.70	−3.542 574 E-4	6.00	−1.728 278 E-6
1.80	−8.053 140 E-4	7.00	−1.162 260 E-6
1.90	−1.435 423 E-3	8.00	−5.968 751 E-7
2.00	−1.772 887 E-3	10.00	−8.519 642 E-8

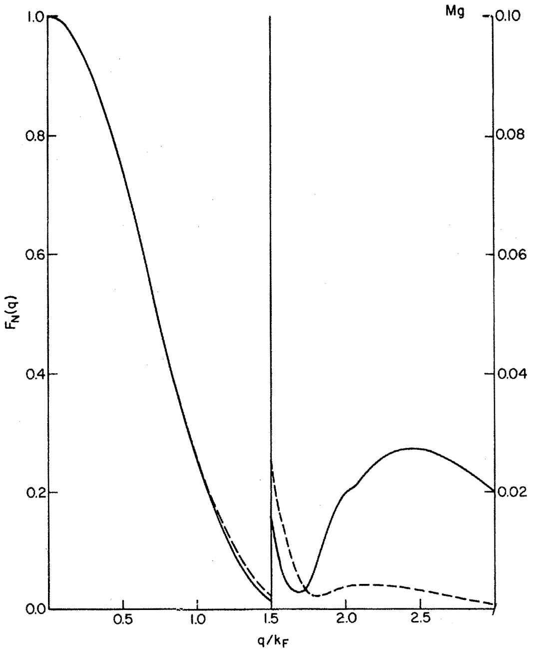

FIG. 2. Normalized energy–wave-number characteristic used in this calculation (solid curve) compared to $F_N(q)$ from Shaw and Pynn (Ref. 7) (dashed curve).

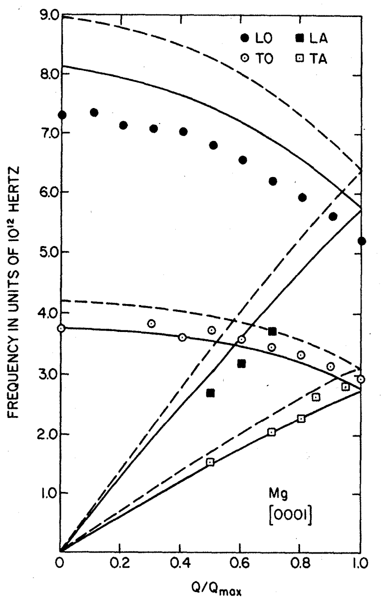

FIG. 3. Theoretical phonon dispersion relations for the three crystallographic directions [0001], [01$\bar{1}$0], and [11$\bar{2}$0] in magnesium. In the first two directions, the curves were computed both with (solid curves) and without (dashed curves) the contribution from conduction-electron exchange. Those branches composed of a single solid curve were not modified perceptibly by the inclusion of conduction-electron exchange. Experimental points in the [0001] and [01$\bar{1}$0] directions are taken from Iyengar *et al.* (Ref. 45), while points in the [11$\bar{2}$0] direction are from Pynn and Squires (Ref. 46).

the Born-Ewald-Fuchs[43,44,38] method for a lattice of point ions immersed in a uniform compensating background of negative charge. For the hcp lattice, the energy per ion obtained from this method is given by

$$E_{es}=\tfrac{1}{2}(Z^*e)^2\left[\frac{4\pi}{\Omega_0}\sum_{\vec{K}}{}'\frac{e^{-K^2/4\eta^2}\cos^2\theta}{K^2}-\frac{2\eta}{\sqrt{\pi}}+\sum_j\sum_{\vec{a}}{}'\frac{\mathrm{erfc}(\eta|\vec{a}+\vec{d}_j|)}{|\vec{a}+\vec{d}_j|}-\frac{\pi}{\eta^2\Omega_0}\right],$$

where $\theta=\frac{1}{2}\vec{K}\cdot\vec{d}_2$, η is a convergence parameter, and the primes over the sums indicate that zero denominators are not to be included.

As in Sec. II E, we shall neglect the ion-ion repulsive contribution to the energy. The electronic or band-structure contribution is calculated by evaluating

$$E_{bs}=\sum_{\vec{q}}{}'|S\vec{q}|^2F(q)\ .$$

III. RESULTS AND DISCUSSION

For the core states $|nl\rangle$, we used wave functions for the Mg^{++} ion; these were computed with the HFS program written by Herman and Skillman,[24] using an unmodified HFS potential. We used these wave functions to calculate the pseudopotential matrix elements and $F(q)$ with (i) the free-electron dielectric function and (ii) the modified dielectric function containing the conduction-electron exchange in the approximation of Eq. (2). Figure 2 shows a plot of the normalized $F(q)$, calculated with $\epsilon^*(q)$, and compared with the $F_N(q)$ from Shaw and Pynn.[7] It is seen that the two functions are in close agreement except in the intermediate region. Since the plot of the energy-wave-number characteristic using the free-electron dielectric function differs only slightly from the $F(q)$ plotted in Fig. 2, we have omitted it from the diagram. Selected values of $F(q)$ are given in Table VI.

The Coulombic contributions to the dynamical matrix were computed by summing over approximately 100 vectors in both real and reciprocal space. Convergence was very rapid with the choice of $\eta=(4/\Omega_0)^{1/3}$. Band-structure contributions were computed by summing over more than 1500 reciprocal-lattice vectors, which, at the very worst, gave convergence to three or four decimal places.

The theoretical phonon frequencies are shown in Fig. 3 for the [0001], the [01$\bar{1}$0], and the [11$\bar{2}$0] directions. Dashed lines refer to the results obtained when conduction-electron exchange is not included in the pseudopotential, while the solid lines are the results that include this interaction. The branches where only a solid line is shown were not sufficiently modified when the Hartree dielectric function was used to show up on the scale of the

TABLE VII. A comparison of the phonon frequencies computed at various symmetry points by Shaw-Pynn (Ref. 7) and King-Cutler. Both calculations include conduction-electron exchange with the Kohn-Sham long-wavelength limit. The symmetry points are described by Shaw and Pynn. All frequencies are in units of 10^{12} Hz.

Symmetry	Shaw-Pynn	King-Cutler	Experiment[a]
Γ_5^+	3.78	4.07	3.70
Γ_3^+	8.10	7.25	7.30
M_1^+	7.63	6.87	6.88
M_2^-	7.28	6.73	6.58
M_4^+	3.73	3.95	3.70
M_3^-	5.66	5.67	5.45
M_3^+	4.26	4.14	4.15
M_4^-	6.52	6.02	6.12
A_3	2.78	3.18	2.94
A_1	5.73	5.35	5.20

[a] References 45 and 46.

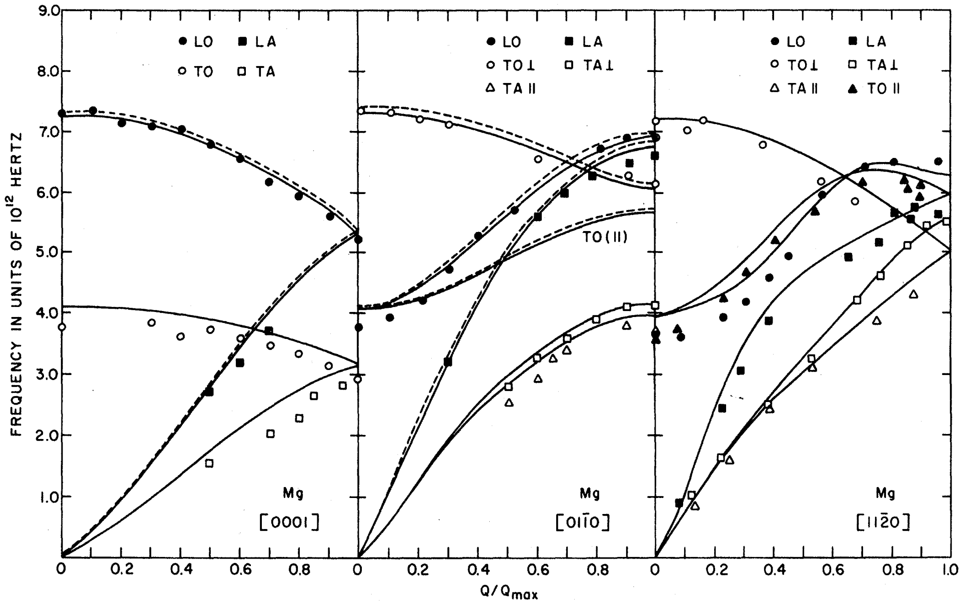

FIG. 4. Theoretical phonon spectrum in the [0001] direction for magnesium, from Shaw and Pynn (Ref. 7). The solid curves are calculated with an approximation for conduction-electron exchange and correlation, using the Kohn-Sham (Ref. 8) long-wavelength limit, while the dashed curves are without this contribution.

figure. As can be seen, the results are surprisingly good, particularly when one considers the first-principles nature of the calculations. For a comparison with a recent OHA quasi-first-principles calculation, we have listed in Table VII our phonon frequencies, together with Shaw and Pynn's[7] results, at symmetry points; in Fig. 4 we have also reproduced SP's curves for the [0001] direction. As can be seen from this figure, the calculation of Shaw and Pynn also shows good agreement. An important obvious difference is the greater effect that the inclusion of the conduction-electron exchange interaction has on the dispersion relations in the SP calculation. This is a result that our calculations do not exhibit[34] (see Fig. 3). This effect may possibly be a consequence of the OHA model potential formulation itself, rather than an intrinsic physical phenomenon. The present dispersion curves for magnesium, as well as previous results for beryllium,[34,23] indicate that the inclusion of conduction-electron exchange does not greatly modify the calculated phonon dispersion relations. This implies that for the HFP method, the choice of an interpolation formula for the conduction-electron exchange and correlation is not very critical to the calculation of accurate phonon spectra. It is natural to ask how one reconciles this with the results from the many recent pseudopotential calculations using different schemes for exchange and correlation. It is recognized that there is as yet no fundamental or unique solution to the exchange and correlation problem at metallic densities. Therefore, one may speculate that for lattice dynamics calculations, the results obtained with the various pseudopotential formulations and schemes for including exchange and correlation interactions in the electron gas are strongly model dependent. We do not know whether similar conclusions concerning exchange and correlation effects obtain when calculating electronic band structures using pseudopotential theory. Calculations are currently in progress to investigate this problem.

TABLE VIII. Components of the total binding energy for magnesium calculated in Ry per ion. All values are computed at the observed c/a ratio.

Component	Value
E_{fe}	0.714 04
E_{bs}	−0.086 76
E_{es}	−2.485 39
Total	−1.858 1
Observed	−1.78

TABLE IX. Contributions to the elastic shear constants of magnesium calculated with the HFP theory. Experimental values are from Slutsky and Garland (Ref. 51), extrapolated to 0 °K, and all values are in units of 10^{12} dynes/cm^2.

Contribution	C	C'	c_{44}
Electrostatic	2.8969	0.3395	0.2010
Band structure	−1.6788	−0.1323	−0.0219
Total	1.2181	0.2072	0.1791
Experimental	1.3552	0.1877	0.1842
Percent difference with experiment (%)	10 low	10 high	3 low

We have also used this same $F(q)$ to calculate the total binding energy, defined as the energy of the metal minus the energies of the isolated ions and electrons.[26] The values of the free-electron energy, the band-structure energy, and the electrostatic energy, calculated at the observed c/a ratio, are listed in Table VIII. The total binding energy calculated in this way compares favorably with the experimental value of 1.78 Ry/ion. We also tried the Pines[47] formula to approximate E_{xc} in the expression for the free-electron energy. This resulted in a theoretical binding energy that was about 5% more negative than when the Gell-Mann and Brueckner[42] expression was used. When the electrostatic energy was calculated as a function of the c/a ratio in steps of $c/a = 0.0005$, we found that the minimum did not occur at the ideal axial ratio, as suggested by Harrison,[48] but rather at $c/a = 1.6355$, in agreement with Cousins.[49]

We have reported elsewhere on a calculation of the elastic shear constants of magnesium using this same pseudopotential,[50] so we will not elaborate on any of the details here. For completeness, however, and to indicate both the utility and consistency of results with this pseudopotential, the values for these shear constants are quoted in Table IX.

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