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Third-Order Elastic Constants of Magnesium. II. Theoretical*

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A theoretical model has been developed to predict the elastic constants of magnesium. The energy density of the metal consisted of a volume-dependent term, an electrostatic term, and a band-structure term which was derived from pseudopotential theory. The pseudopotential used was the local one proposed by Ashcroft and used by Suzuki *et al.* in calculating the elastic constants of the alkali metals. There were two adjustable parameters. One is the core radius r_c and the other is a shear-independent term adjusted to give equilibrium at the observed atomic volume. The calculations were carried out for five different core radii in order to determine the r_c which gives the best agreement between theory and experiment. Both the Hartree dielectric function and a modified dielectric function were used. The results were found to be rather insensitive to whichever dielectric function is used. From a comparison of the calculated elastic constants with experiment, it was found that the best agreement was obtained for $r_c = 1.358\ a_0$ (and the modified dielectric function). There was only a slight preference, however, over $r_c = 1.38 a_0$ (and the Hartree dielectric function). The core radius determined from elastic-constant calculations was found to be in good agreement with the values obtained by other investigators from a comparison of theory with experiment for electronic properties, such as the resistivity of liquid magnesium. Thus the same pseudopotential predicts both mechanical and electronic properties of magnesium. Because magnesium exists in the nonprimitive hcp structure, a macroscopic strain gives rise to interlattice displacements, i.e., internal strains. The internal-strain parameter has been calculated by requiring the energy density of the strained state to be a minimum. It was seen that internal-strain contributions to the Brugger elastic constants, although small, did improve the over-all agreement between theory and experiment.

I. INTRODUCTION

Recently Suzuki *et al.* have used a pseudopotential method to calculate the elastic constants of the alkali metals[1] (monovalent) and of aluminum[2] (trivalent). Their results are in excellent agreement with experiment for the monovalent metals and in fair agreement with experiment for aluminum. It should be noted, however, that a complete set of third-order constants has not yet been determined experimentally for any of the alkali metals. Thus Suzuki *et al.* could only compare their results with the experimental values of the second-order constants and of the hydrostatic-pressure derivatives of the second-order constants. The calculated third-order constants of aluminum could be compared directly with the experimental values obtained by Thomas.[3]

It would be interesting to see how successful the method of Suzuki *et al.* is in predicting the elastic constants of a divalent simple metal. A good candidate for this approach seems to be magnesium, since it has no *d* electrons, and its ion cores are known to be small. The choice of magnesium also will introduce features that are absent from the work of Suzuki *et al.* The simple metals which they considered were cubic with one atom per unit cell. Magnesium, however, crystallizes in the hcp structure, which has a basis of two atoms. The atoms in a hcp structure are not at centers of symmetry. Therefore elastic deformations will, in general, induce internal strains, since the structure is nonprimitive. The internal strain is such as to make the energy density a minimum for the given external elastic strain; i.e., if E is the energy density, η the external strain, and w the induced internal strain, then w is found from $(\partial E/\partial w)_\eta = 0$. In addition, the method can be used to calculate the equilibrium value of c/a.

Recently Cousins[4] calculated electrostatic and repulsive ion-ion contributions to the elastic shear constants of hexagonal metals for various c/a ratios. In magnesium there is very little core overlap, and repulsive ion-ion effects may be neglected. Cousins's results are in exact agreement with our electrostatic calculations if a sign is changed in one of his results.[5] More recently, Cousins[6] and King and Cutler[7] have employed pseudopotential methods to calculate the three second-order shear constants of magnesium. However, they did not calculate the complete set of second- and third-order constants. A comparison of their results with ours will be presented at the end of this paper.

In Sec. II, we discuss the strain parameters to be used in the elastic-constant calculations. In Sec.

III, a pseudopotential model is used to calculate the second- and third-order elastic constants of magnesium, and comparisons with the experimental results of the preceding paper[8] are presented. A summary and conclusions are given in Sec. IV.

II. STRAIN PARAMETERS

At $T = 0\,^{\circ}\mathrm{K}$, and in the absence of zero-point vibrations, the elastic constants are related to the energy per unit undeformed volume E through the expression

$$c_{ijklmn\ldots} = \left(\frac{\partial^n E}{\partial \eta_{ij}\, \partial \eta_{kl}\, \partial \eta_{mn} \cdots} \right)_{\eta=0} . \tag{1}$$

The above elastic constant is of the type defined by Brugger.[9] η_{ij} is a component of the Lagrangian strain tensor and is found as follows. If $\vec{x}$ is the initial coordinate of a particle, and $\vec{x}\,'$ the coordinate in the strained state, then $\eta_{ij} = \frac{1}{2}(J_{ik} J_{jk} - \delta_{ij})$, where $J_{ik} = (\partial x_k{}')/\partial x_i$ and δ_{ij} is the Kronecker δ. The subscript refers to the Cartesian component of a vector, and repeated indices are to be summed. A knowledge of the lattice energy E will thus provide the elastic constants upon differentiation with respect to the appropriate strain parameters.

Experimental elastic constants are usually expressed in terms of the Brugger constants. However, to facilitate the calculations, strains similar to those originally used by Fuchs[10] are employed here. This does not present any difficulty in comparing with experiment, since the Fuchs constants are simply linear combinations of the Brugger constants.

The strains to be used consist of a v strain, corresponding to a homogeneous expansion or contraction of the crystal, and of three volume-conserving shear strains to be called ϵ, γ, and e. These strains offer two computational advantages over the Brugger-type strains. The first advantage is that when taking derivatives with respect to a shear strain, one need not be concerned with energy terms which depend only on volume. The second advantage is that these strains reduce the number of elastic constants for which internal-strain contributions must be calculated. It will be seen that internal strains occur only for the e strain. The strain parameters are described as follows.

1. ϵ *Strain*

The ϵ strain contracts the hexagonal base uniformly and expands the c axis such that volume is conserved. Thus only the c/a ratio is changed:

$$x_1' = (1+\epsilon)^{-1/2} x_1 , \quad x_2' = (1+\epsilon)^{-1/2} x_2 , \quad x_3' = (1+\epsilon) x_3 .$$

x_1 and x_2 are shown in Fig. 1; the prime refers to the strained state.

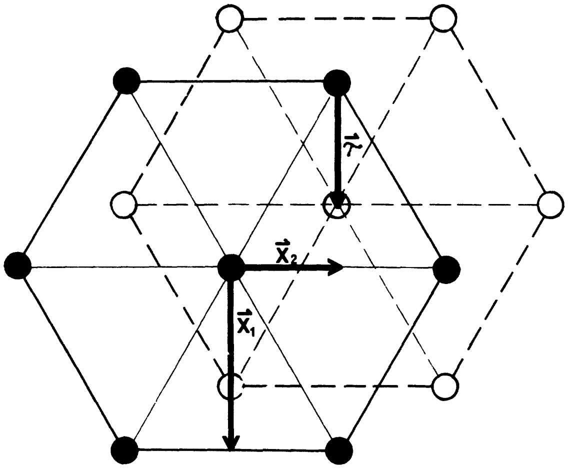

FIG. 1. Coordinate system for the hcp structure. $\vec{x}_3$ is parallel to the c axis, i.e., out of the paper. $\vec{\tau}$ may be written as $\vec{\tau} = \frac{2}{3}\vec{x}_1 + \frac{1}{2}\vec{x}_3$.

2. γ *Strain*

The γ strain tilts the c axis by an angle $\tan^{-1}\gamma$ and leaves the base undeformed. Volume is again conserved:

$$x_1' = x_1 , \quad x_2' = x_2 + \gamma x_3 , \quad x_3' = x_3 .$$

3. e *Strain*

The e strain expands the x_1 axis and contracts the x_2 axis such that the basal area remains unchanged. The c axis is not strained and volume is conserved:

$$x_1' = (1+e)^{1/2} x_1 , \quad x_2' = (1+e)^{-1/2} x_2 , \quad x_3' = x_3 .$$

4. v *Strain*

The v strain contracts or expands all the axes uniformly. Volume is not conserved, but the basal plane retains its hexagonal shape:

$$x_1' = v^{1/3} x_1 , \quad x_2' = v^{1/3} x_2 , \quad x_3' = v^{1/3} x_3 .$$

The ratio of the volume in the strained state to the volume in the unstrained state is simply v.

The relationships between the Fuchs constants and the Brugger elastic constants for cubic crystals have been discussed by Suzuki *et al.*[1] The relationships for hcp structures are summarized in Table I. In this table, as well as in the remainder of this paper, the Voigt notation is used to denote the Brugger elastic constants, i.e.,

$$c_{ijkl\cdots} = c_{IJ\cdots} ,$$

where ij's and I's are related by $11 \sim 1$, $22 \sim 2$, $33 \sim 3$, $23 \sim 4$, $31 \sim 5$, and $12 \sim 6$.

Our choice of Fuchs constants is not unique, but

TABLE I. Relationships between Fuchs and Brugger constants for hcp structures.

$$\frac{\partial^2 E}{\partial \epsilon^2} = \tfrac{1}{2}(c_{11} + c_{12} + 2c_{33} - 4c_{13})$$

$$\frac{\partial^2 E}{\partial \gamma^2} = c_{44}, \quad \frac{\partial^2 E}{\partial e^2} = \tfrac{1}{2}(c_{11} - c_{12}) = c_{66}$$

$$\frac{\partial^2 E}{\partial v^2} = \tfrac{1}{9}(2c_{11} + 2c_{12} + 4c_{13} + c_{33})$$

$$\frac{\partial^2 E}{\partial \epsilon \partial v} = \tfrac{1}{3}(c_{13} + c_{33} - c_{11} - c_{12})$$

$$\frac{\partial^3 E}{\partial \epsilon^3} = 9 \frac{\partial^2 E}{\partial \epsilon\, \partial v} + \tfrac{1}{4}(- 2c_{111} + c_{222} - 3c_{112} + 6c_{113} - 12c_{133} + 4c_{333} + 6c_{123})$$

$$\frac{\partial^3 E}{\partial e^3} = - 3c_{66} + \tfrac{1}{2}(c_{111} - c_{222})$$

$$\frac{\partial^3 E}{\partial v^3} = -\frac{\partial^2 E}{\partial v^2} + \tfrac{1}{27}(4c_{111} - 2c_{222} + 6c_{112} + 6c_{113} + 6c_{133} + c_{333} + 6c_{123})$$

$$\frac{\partial^3 E}{\partial \epsilon\, \partial v^2} = \frac{\partial^2 E}{\partial \epsilon\, \partial v} + \tfrac{1}{9}(- 2c_{111} + c_{222} - 3c_{112} + 3c_{133} + c_{333})$$

$$\frac{\partial^3 E}{\partial v\, \partial \epsilon^2} = 3 \frac{\partial^2 E}{\partial v^2} + \frac{4}{3} \frac{\partial^2 E}{\partial \epsilon^2} + \tfrac{1}{6}(2c_{111} + 3c_{112} - 3c_{113} - c_{222} - 3c_{123} + 2c_{333})$$

$$\frac{\partial^3 E}{\partial v\, \partial \gamma^2} = \tfrac{1}{3}(2c_{13} + c_{33}) + \tfrac{4}{3}c_{44} + \tfrac{1}{3}(c_{144} + c_{155} + c_{344})$$

$$\frac{\partial^3 E}{\partial \epsilon\, \partial \gamma^2} = (c_{33} - c_{13} + c_{44}) + \tfrac{1}{2}(- c_{144} - c_{155} + 2c_{344})$$

$$\frac{\partial^3 E}{\partial e\, \partial \gamma^2} = - c_{44} + \tfrac{1}{2}(c_{144} - c_{155})$$

$$\frac{\partial^3 E}{\partial \epsilon\, \partial e^2} = \tfrac{1}{2}(2c_{13} - c_{11} - c_{12}) - 2c_{66} + \tfrac{1}{4}(- c_{222} + c_{112} + 2c_{113} - 2c_{123})$$

$$\frac{\partial^3 E}{\partial v\, \partial e^2} = \tfrac{1}{3}(c_{11} + c_{12} + c_{13}) + \frac{4}{3}c_{66} + \frac{1}{6}(c_{222} - c_{112} + c_{113} - c_{123})$$

represents all the independent second- and third-order elastic constants of a hcp crystal. It should be noted that the ϵ, e, and v strains commute; thus the order in which they are applied is immaterial. γ, however, does not commute with ϵ or e. The order does not matter if one is consistent throughout. When combining γ with ϵ or e, we have always applied γ last.

III. PSEUDOPOTENTIAL MODEL

Following Suzuki *et al.*,[1,2] the energy of the metal may be written as a sum of three terms: a volume-dependent term E_v, which includes the Fermi, exchange, and correlation energies; an electrostatic term E_c, which is the Coulomb energy of positive point charges arranged on a lattice and embedded in a uniform sea of conduction electrons; and a band-structure term E_{BS}, which represents the deviation of the electron energy from that of free electrons. Throughout this work, all energies will be in units of rydbergs per electron and all lengths in atomic units. The volume-dependent energy may be written as

$$E_v = 0.6\, k_F^2 - 0.916/r_s - (0.115 - 0.031 \ln r_s) . \quad (2)$$

r_s is given by

$$\tfrac{4}{3}\, \pi r_s^3 = V_0/Z , \quad (3)$$

where V_0 is the atomic volume and Z the valence. k_F is the radius of the free-electron Fermi sphere given by

$$k_F^3 = 3\pi^2 Z/V_0 . \quad (4)$$

According to the Ewald-Fuchs[11] method, E_c may be written as

$$E_c = \frac{Z^{2/3}}{r_s}\left(\frac{3}{4\pi}\right)^{1/3}\left[\sum_l{}' \phi_{-1/2}\left(\frac{\vec{R}_l^2}{V_0^{2/3}}\pi\right) + \sum_l \phi_{-1/2}\left(\frac{|\vec{R}_l + \vec{\tau}|^2}{V_0^{2/3}}\pi\right) + \sum_l{}' \cos^2(\tfrac{1}{2}\vec{q}_l \cdot \vec{\tau})\phi_0\left(\frac{V_0^{2/3}\vec{q}_l^{\,2}}{4\pi}\right) - 3\right] . \quad (5)$$

In the above equation, $\vec{R}_l$ is a lattice vector; $\vec{\tau}$ is the position vector of the second basis atom; $\vec{q}_l$ is a reciprocal-lattice vector, and $\phi_m(x) \equiv \int_1^\infty dt\, t^m e^{-xt}$. The prime on a sum means the $l = 0$ term is omitted.

The perturbation or band-structure energy term E_{BS} is calculated by introducing a simple local pseudopotential and applying second-order perturbation theory. The pseudopotential to be used is the one originally proposed by Ashcroft[12] and Ashcroft and Langreth[13] and used by Suzuki *et al.*[1] The effective potential vanishes inside the closed ion core and is pure Coulombic outside the core. E_{BS} is then given by

$$E_{\mathrm{BS}} = \frac{\alpha Z}{V_0} - \frac{k_F}{3\pi} \sum_q{}' \eta^{-2} \cos^2(\tfrac{1}{2}\vec{q} \cdot \vec{\tau}) \cos^2(q r_c) \times \frac{\epsilon(\eta, k_F) - 1}{\epsilon(\eta, k_F)} . \quad (6)$$

$\vec{q}$ is a reciprocal-lattice vector, and $\eta = q/2k_F$; r_c is the core radius of the ion, and $\epsilon(\eta, k_F)$ is the Hartree dielectric function given by

$$\epsilon(\eta, k_F) = 1 + g(\eta)/2\pi k_F a_0 , \quad (7)$$

where a_0 is the Bohr radius and

$$g(\eta) = \frac{1}{\eta^2} + \frac{1 - \eta^2}{2\eta^3} \ln\left|\frac{1 + \eta}{1 - \eta}\right| . \quad (8)$$

α is found from first-order perturbation theory to be

$$\alpha = 4\pi r_c^2 \ . \qquad (9)$$

E_v depends only on the atomic volume, and thus this term only contributes to two Fuchs constants $\partial^2 E/\partial v^2$ and $\partial^3 E/\partial v^3$. All shear derivatives of E_v are zero. For a v strain, $k_F' = v^{-1/3} k_F$ and $r_s' = v^{1/3} r_s$. v derivatives of E_v are easily performed.

The derivatives of E_c with respect to the Fuchs strains are readily taken. Any lattice vector may be written as (see Fig. 1)

$$\vec{R}_l = l_1 \vec{x}_1 + l_2 \vec{x}_2 + l_3 \vec{x}_3 \ ,$$

where $l_1 + l_2 =$ even integer and $x_1 = \frac{1}{2}\sqrt{3}\, a$, $x_2 = \frac{1}{2} a$, and $x_3 = c$. Similarly, any reciprocal-lattice vector may be expressed as

$$\vec{q}_l = l_1 \vec{G}_1 + l_2 \vec{G}_2 + l_3 \vec{G}_3 \ ,$$

with the same restriction on $l_1 + l_2$. Here $G_1 = \pi/x_1$, $G_2 = \pi/x_2$, and $G_3 = 2\pi/x_3$. For a given Fuchs strain, one knows exactly how the lattice and reciprocal-lattice vectors deform. For example, for a v strain,

$$\vec{R}_l' = v^{1/3}\vec{R}_l \ , \quad \vec{q}_l' = v^{-1/3}\vec{q}_l \ , \quad V_0' = v V_0 \ .$$

The prime denotes the quantity in the strained state. For an ϵ strain,

$$\vec{R}_l' = l_1 (1+\epsilon)^{-1/2} \vec{x}_1 + l_2 (1+\epsilon)^{-1/2} \vec{x}_2 + l_3 (1+\epsilon) \vec{x}_3 \ ,$$

$$\vec{q}_l' = l_1 (1+\epsilon)^{1/2} \vec{G}_1 + l_2 (1+\epsilon)^{1/2} \vec{G}_2 + l_3 (1+\epsilon)^{-1} \vec{G}_3 \ ,$$

$$V_0' = V_0 \ .$$

The expression for the band-structure energy is a function of η and k_F. For a v strain, η does not change, since

$$\eta' = \frac{q'}{2k_F'} = \frac{v^{-1/3} q}{2 v^{-1/3} k_F} = \frac{q}{2k_F} = \eta \ .$$

For a shear strain, k_F does not change, since it only depends on volume. Thus one need only take derivatives of E_{BS} with respect to η and k_F. For example, we have

$$\frac{\partial E_{\mathrm{BS}}}{\partial v} = \frac{\partial E_{\mathrm{BS}}}{\partial k_F} \frac{\partial k_F}{\partial v} \qquad (10)$$

and

$$\frac{\partial E_{\mathrm{BS}}}{\partial \epsilon} = \frac{\partial E_{\mathrm{BS}}}{\partial \eta} \frac{\partial \eta}{\partial \epsilon} \ . \qquad (11)$$

It is assumed that the core radius r_c does not change during deformation. In all band-structure sums, we sum out to $(l_1, l_2, l_3) = (18, 10, 17)$, which corresponds to $\eta \sim 7$.

As seen above, one knows how $\vec{R}_l$ deforms under a homogeneous deformation such as a Fuchs strain. However, the hcp structure is nonprimitive, consisting of two interpenetrating hexagonal sublattices that are separated by a vector $\vec{\tau}$, and one does not know how $\vec{\tau}$ will deform. If the components of $\vec{R}_l$ deform as

$$(\vec{R}_l')_i = J_{ik} (\vec{R}_l)_k \ , \qquad (12)$$

then, for a general homogeneous deformation,[14]

$$(\vec{R}_l' + \vec{\tau}')_i = J_{ik} (\vec{R}_l + \vec{\tau})_k + (\vec{w})_i \ . \qquad (13)$$

$\vec{w}$ is referred to as the inner displacement vector. The homogeneous strain described by the matrix J_{ik} has induced an internal strain between the two sublattices. $\vec{w}$ is found by requiring the energy density of the homogeneously deformed state to be a minimum.

Certain deformations have the necessary symmetry so that there is no internal strain. Floyd and Kleinman[15] have shown that $\vec{w}$ vanishes for strains of the c axis and for strains which do not distort the base from being a regular hexagon. They have also shown that for a general strain, the vector $\vec{\tau}$ between the two sublattices will be such that it tends to reequalize the nearest-neighbor distances. In terms of the matrix J_{ik}, they have shown that $\vec{w}$ has a component along the x_1 axis only if $J_{11} \neq J_{22}$; that $\vec{w}$ has a component along the x_2 axis only if $J_{12} \neq 0$; and that $\vec{w}$ never has a component along the x_3 axis.

All four of our Fuchs strains are such that $J_{12} = J_{21} = 0$. In addition the v, ϵ, and γ strains do not distort the regular hexagonal shape of the basal plane, i.e., $J_{11} = J_{22}$. The only Fuchs strain which will give rise to a nonvanishing internal strain is the e strain, for which $J_{11} \neq J_{22}$. $\vec{w}$ will then have a component only along the x_1 axis.

When calculating an elastic constant involving the e strain, it will be necessary to include the contributions from $\vec{w}$. For an e strain, the lattice and reciprocal-lattice vectors will deform according to

$$\vec{R}_l' = l_1 (1+e)^{1/2} \vec{x}_1 + l_2 (1+e)^{-1/2} \vec{x}_2 + l_3 \vec{x}_3 \ ,$$

$$\vec{q}_l' = l_1 (1+e)^{-1/2} \vec{G}_1 + l_2 (1+e)^{1/2} \vec{G}_2 + l_3 \vec{G}_3 \ ,$$

and

$$\vec{\tau}' = [(1+e)^{1/2} \tau_1 + w]\, \hat{x}_1 + (1+e)^{-1/2} \tau_2 \hat{x}_2 + \tau_3 \hat{x}_3 \ ,$$

where

$$\tau_1 = \tfrac{2}{3} x_1, \quad \tau_2 = 0, \quad \tau_3 = \tfrac{1}{2} x_3, \quad \hat{x}_i \equiv \vec{x}_i / |\vec{x}_i| \ .$$

Differentiations with respect to e are readily taken once w is known. Obviously w is a function of e, so that one may perform a power-series expansion:

$$w = Ae + Be^2 + \cdots . \qquad (14)$$

It will be shown below that only the coefficient A is needed in the calculation of second- and third-order elastic constants.

If $E(e, w)$ is the energy density, then

$$\frac{dE}{de} = \left(\frac{\partial E}{\partial e}\right)_w + \left(\frac{\partial E}{\partial w}\right)_e \frac{\partial w}{\partial e} = E_e + E_w w_e \ , \tag{15}$$

where the subscripts refer to partial derivatives. As stated earlier, $E_w = (\partial E/\partial w)_e$ must be zero for all values of e.

Since $E_w \equiv 0$, one must then have

$$\frac{d}{de} E_w \equiv 0 = E_{ew} + E_{ww} w_e \ . \tag{16}$$

Equation (16) is identically zero for all e. Since $(w_e)_{e=0} = A$, one finds that

$$A = -(E_{ew}/E_{ww})_{e=0} \ . \tag{17}$$

Differentiating Eq. (15) with respect to e and setting $E_w = 0$, one obtains

$$\frac{d^2E}{de^2} = E_{ee} + E_{ew} w_e \ . \tag{18}$$

Since the elastic constants are evaluated in the unstrained state,

$$\left(\frac{d^2E}{de^2}\right)_0 = (E_{ee})_0 + A(E_{ew})_0 \ . \tag{19}$$

The last term in Eq. (19) is the internal-strain contribution to the Fuchs constant.

By differentiating Eqs. (18) and (16) with respect to e, one obtains

$$\frac{d^3E}{de^3} = E_{eee} + 2E_{eew} w_e + E_{eww} w_e^2 + E_{ew} w_{ee} \ , \tag{20}$$

$$0 = E_{eew} + 2E_{eww} w_e + E_{www} w_e^2 + E_{ww} w_{ee} \ . \tag{21}$$

Multiplying Eq. (21) by w_e and adding this to Eq. (20) gives

$$\frac{d^3E}{de^3} = E_{eee} + 3E_{eew} w_e + 3E_{eww} w_e^2 + E_{www} w_e^3 + w_{ee}(w_e E_{ww} + E_{ew}) \ . \tag{22}$$

But the coefficient of w_{ee} is identically zero by Eq. (16). Evaluating Eq. (22) in the unstrained state, one finds that

$$\left(\frac{d^3E}{de^3}\right)_0 = (E_{eee})_0 + 3A(E_{eew})_0 + 3A^2(E_{eww})_0 + A^3(E_{www})_0 \ . \tag{23}$$

Equation (23) is exact. One sees that only the linear term of Eq. (14) is needed. The other elastic constants involving e are $d^3E/dv\,de^2$, $d^3E/d\epsilon\,de^2$, and $d^3E/de\,d\gamma^2$. It can easily be shown that

$$\left(\frac{d^3E}{dv\,de^2}\right)_0 = (E_{vee})_0 + 2A(E_{vwe})_0 + A^2(E_{vww})_0 \ , \tag{24}$$

$$\left(\frac{d^3E}{d\epsilon de^2}\right)_0 = (E_{\epsilon ee})_0 + 2A(E_{\epsilon we})_0 + A^2(E_{\epsilon ww})_0 \ , \tag{25}$$

$$\left(\frac{d^3E}{de\,d\gamma^2}\right)_0 = (E_{e\gamma\gamma})_0 + A(E_{w\gamma\gamma})_0 \ . \tag{26}$$

The first term in each expression is the contribution to the elastic constant assuming no internal strain, i.e., $A = 0$.

There are one second-order (d^2E/de^2) and four third-order Fuchs constants (d^3E/de^3, $d^3E/dv\,de^2$, $d^3E/d\epsilon\,de^2$, and $d^3E/de\,d\gamma^2$) which involve internal strain. When the Brugger constants are expressed in terms of the Fuchs constants, it is seen that two second-order Brugger constants (c_{11} and c_{12}) and seven third-order constants ($c_{111}, c_{222}, c_{112}, c_{123}, c_{113}, c_{144}$, and c_{155}) involve internal strain.

Calculations have been completed for five values of the core radius, namely, $r_c = (1.22,\ 1.34,\ 1.358,\ 1.38,$ and $1.50)a_0$. The value $r_c = 1.38a_0$ is near the value of $1.39a_0$ determined by Ashcroft and Langreth[13] from a comparison of theory and experiment for the resistivity of liquid magnesium. The value $r_c = 1.358a_0$ was found by Shyu and Gaspari[16] from fitting the first zero of the Ashcroft pseudopotential form factor to that of the Heine-Abarenkov "model"[17] pseudopotential. The other values of r_c were chosen to provide a wide range of core radii to be used in the later comparison of theory with experiment.

In addition to using the Hartree dielectric function, calculations have been performed using a modified[16, 18-21] dielectric function. The modified function takes into account correlation and exchange effects in the screening of the electrons. If one defines $H(q) = \epsilon(q)/[\epsilon(q) - 1]$, then for the Hartree dielectric function

$$H = 1 + 2\pi k_F a_0 / g(\eta) \ , \tag{27}$$

where $g(\eta)$ = is given by Eq. (8). H^{-1} directly enters Eq. (6) for the expression for E_{BS}. For the modified dielectric function, one has

$$H = 1 + 2\pi k_F a_0 / g(\eta) - q^2/2(q^2 + \beta k_F{}^2) \ . \tag{28}$$

Two forms of β were used: The first was introduced by Sham[18] and used by Shyu and Gaspari,[16,19,20] where $\beta = 1 + 2/(\pi k_F a_0)$; the second form was used by Wallace,[21] where $\beta = 2\pi k_F a_0/(0.158 + \pi k_F a_0)$. The elastic-constant calculations were found to be extremely insensitive to whichever form of β is used. This finding is an agreement with the lattice dynamic calculations of King and Cutler.[7]

Using the experimental[22] atomic volume of magnesium, we have determined the equilibrium c/a ratios for the five core radii. The results using both the Hartree and the modified dielectric func-

TABLE II. Equilibrium values of c/a and internal-strain parameter A for various values of r_c. The experimental value of c/a for magnesium is 1.6228.[a] A is in units of the lattice parameter a.

r_c	c/a		A	
(units of a_0)	Hartree	Modified	Hartree	Modified
1.22	1.6413	1.6414	0.326	0.223
1.34	1.6337	1.6316	0.374	0.335
1.358	1.6327	1.6304	0.383	0.350
1.38	1.6315	1.6291	0.394	0.368
1.50	1.6259	1.6236	0.461	0.460

[a] Reference 22.

tions are presented in Table II. Each c/a was found by numerically solving $\partial E/\partial\epsilon = 0$. The volume-dependent energy E_v does not enter here. It should be noticed that over our range of core radii c/a does not differ much from the ideal value of 1.633. Thus the procedure will not be successful when applied to a hcp metal such as zinc, for which $c/a = 1.856$.

Knowing c/a for each r_c, we then calculated the internal-strain parameter A discussed earlier. Again only the Coulomb and band-structure energies contribute here. The results are given in Table II. In the one-orthogonalized-plane-wave (1-OPW) approximation, for which the band-structure energy is neglected, it is found that $A = 0.8575a$, in agreement with the value given by Floyd and Kleinman.[15] Inclusion of the band structure considerably reduces the internal strain, as can be seen in Table II.

Account must be taken of another equilibrium condition, namely, that $\partial E/\partial_v = 0$. As will be seen shortly, the core radius which gives the best agreement of the calculated elastic constants with experiment is $r_c = 1.358a_0$. Using this core radius, the value of the atomic volume for which $\partial E/\partial_v = 0$ was found to be 30% lower than the experimental value. In order to have equilibrium at the observed atomic volume, it is necessary to adjust one of the parameters. Suzuki *et al.*,[1] as well as Ashcroft and Langreth,[13] have chosen to adjust the parameter α of Eq. (6). The same procedure is adopted here.

It will be seen that with $r_c = 1.358a_0$, four of the five second-order Fuchs elastic constants are in good agreement with experiment. The other constant $(\partial^2E/\partial v^2)$ is only in fair agreement with experiment; this is the only second-order constant which contains a contribution from E_v. Instead of adjusting α, we have tried to adjust independently the Fermi, exchange, and correlation energies, but the results of these adjustments all resulted in a poorer value for $\partial^2E/\partial v^2$. Since an adjustment is necessary, the α adjustment seems best in that it results in a better value for $\partial^2E/\partial v^2$. The pseudopotential method sucessfully predicts the thirteen second- and third-order elastic constants for which there are no contributions from the volume-dependent energy E_v. The other two constants, namely, $\partial^2E/\partial v^2$ and $\partial^3E/\partial v^3$, do depend on E_v. We are thus in agreement with Suzuki *et al.* in supposing that the reason for the failure of the binding energy to be a minimum at the observed atomic volume is mainly due to uncertainties in the volume-dependent energy term E_v.

The results obtained by requiring $\partial E/\partial v = 0$ at the observed atomic volume are given in Table III. Since four second-order Brugger constants (all but c_{44}) depend on $\partial^2E/\partial v^2$, a comparison with experiment is not shown for them. Such a comparison would be distorted by the effect of an inaccurate value for $\partial^2E/\partial v^2$. For the same reason, a comparison of the pressure derivatives of the elastic constants is not given, since they are dependent upon $(\partial^2E/\partial v^2)^{-1}$. (A fair comparison might be made by using the experimental value of $\partial^2E/\partial v^2$ in the determination of the second-order Brugger constants and their pressure derivatives. Such a comparison is given later.)

The purpose of Table III is to determine the core radius r_c for which the calculated elastic constants best agree with experiment. The results obtained by using both the Hartree and the modified dielectric function are listed. It can be seen that the results are rather insensitive to whichever dielectric function is used. King and Cutler[7] have also found that the choice of a particular dielectric function is not significant. It appears that $r_c = 1.358a_0$ (with the modified dielectric function) gives the best over-all agreement with experiment, although the preference over choosing $r_c = 1.38a_0$ (with the Hartree dielectric function) is very slight. For $r_c = 1.358a_0$, one obtains $\alpha = 27.91a_0^2$, compared to the theoretical value of $4\pi r_c^2 = 23.17a_0^2$. The agreement of α with $4\pi r_c^2$ is fair; a better expression for E_v may improve the agreement. Using $r_c = 1.358a_0$ and the modified dielectric function, the binding energy $E = -0.886$ Ry/electron, which is in reasonable agreement with the experimental value of[13] -0.890 Ry/electron.

The values in Table III include the contributions from internal strain. So that one may see the effect of the internal strain on the elastic constants, the calculated values found both by including and neglecting internal strain have been listed in Table IV. The values shown are those obtained by using $r_c = 1.358a_0$ and the modified dielectric function, since the best agreement with experiment was obtained with these parameters. It can be seen that internal-strain contributions to the Brugger constants are small, but do improve the over-all agreement with experiment.

So that one may see the relative contribution of the electrostatic and band-structure energy terms to the elastic constants, the separate contributions have been listed in Table V. The constants which

TABLE III. Elastic-constant calculations using a pseudopotential method. Entries are in units of 10^{12} dyn cm^{-2}.

	Calculated values										
	$r_c = 1.22a_0$		$1.34a_0$		$1.358a_0$		$1.38a_0$		$1.50a_0$		
	Har.	Mod.	Har.	Mod.	Har.	Mod.	Har.	Mod.	Har.	Mod.	Expt. values[a]
$\frac{\partial^2 E}{\partial \epsilon^2}$	0.502	0.420	0.768	0.742	0.817	0.801	0.880	0.875	1.277	1.340	0.728
$\frac{\partial^2 E}{\partial e^2}$	0.121	0.116	0.189	0.196	0.200	0.209	0.215	0.226	0.297	0.317	0.202
$\frac{\partial^2 E}{\partial v^2}$	0.262	0.237	0.295	0.275	0.303	0.284	0.313	0.296	0.392	0.386	0.382
$\frac{\partial^2 E}{\partial \gamma^2}$	0.091	0.088	0.162	0.171	0.174	0.186	0.191	0.205	0.292	0.320	0.198
$\frac{\partial^2 E}{\partial \epsilon\, \partial v}$	−0.006	−0.008	−0.009	−0.009	−0.009	−0.009	−0.009	−0.009	−0.010	−0.009	−0.002
c_{133}	−0.98	−0.85	−1.16	−1.07	−1.20	−1.11	−1.26	−1.17	−1.63	−1.60	−0.86
c_{333}	−4.10	−4.14	−5.70	−5.99	−5.99	−6.32	−6.35	−6.73	−8.66	−9.31	−7.26
c_{111}	−4.64	−4.64	−6.24	−6.42	−6.50	−6.71	−6.83	−7.06	−8.63	−8.97	−6.63
c_{112}	−1.30	−1.15	−1.68	−1.60	−1.76	−1.69	−1.87	−1.83	−2.71	−2.84	−1.78
c_{113}	0.14	0.10	0.42	0.46	0.47	0.51	0.52	0.57	0.81	0.91	0.30
c_{222}	−5.81	−5.66	−7.94	−8.05	−8.30	−8.46	−8.76	−8.97	−11.54	−12.05	−8.64
c_{123}	−0.21	−0.12	−0.35	−0.30	−0.38	−0.33	−0.42	−0.38	−0.71	−0.72	−0.76
c_{144}	−0.31	−0.24	−0.39	−0.35	−0.41	−0.37	−0.43	−0.40	−0.62	−0.63	−0.30
c_{155}	−0.30	−0.44	−0.47	−0.60	−0.50	−0.62	−0.53	−0.65	−0.67	−0.77	−0.58
c_{344}	−1.25	−1.20	−1.76	−1.79	−1.85	−1.90	−1.96	−2.02	−2.64	−2.79	−1.93

[a]Reference 22.

have a contribution from the volume-dependent energy term have not been listed. It can be seen that $\partial^2 E/\partial\gamma^2 = c_{44}$ is determined primarily from the electrostatic energy, but for most of the other constants the band-structure contribution is large. This was not so in the case of the alkali[1] ($Z = 1$) metals. For aluminum[2] ($Z = 3$), however, the band-structure effects were also found to be large. Harrison[17] has also noticed the increase in band-structure contributions for higher valence. He has noted that quantitative calculations become more difficult for higher valence, since the results are increasingly sensitive to errors in the band-structure energy. That this is true has now been borne out by the elastic-constant calculations for the $Z = 1$, 2, and 3 metals. Agreement with experiment was excellent for $Z = 1$ (alkali metals), good for $Z = 2$ (Mg, present work), and fair for $Z = 3$ (Al).

If one used the experimental value of $\partial^2 E/\partial v^2$, instead of the calculated value, together with the calculated values of the four other second-order Fuchs constants, the five second-order Brugger constants listed in Table VI are obtained. Also listed are the resulting pressure derivatives of the second-order constants. For the latter, the calculated values of the third-order Brugger constants were used (Table IV). The agreement with experiment is very good for the second-order constants and for dc_{66}/dP, but only fair (~ 20%) for the other pressure derivatives. It was found, however, that better (~ 10%) agreement of these pressure derivatives with experiment could be obtained by also using the experimental value of $\partial^3 E/\partial v^3$. This is another indication that the volume-dependent energy term is not known as accurately as the other terms.

So that one may see the effect of using different pseudopotentials, in Table VII we have compared our second-order shear constants with those calculated by Cousins[6] and by King and Cutler.[7] Our results are listed for $r_c = 1.358a_0$ with the modified dielectric function. Cousins's results are obtained

TABLE IV. Internal-strain contributions to the third-order elastic constants of Mg. Entries are in units of 10^{12} dyn cm^{-2}.

	Calculated values		
	Without internal strain	With internal strain	Expt. values[a]
c_{133}	−1.11	−1.11	−0.86
c_{333}	−6.32	−6.32	−7.26
c_{111}	−7.31	−6.71	−6.63
c_{112}	−1.35	−1.69	−1.78
c_{113}	0.12	0.51	0.30
c_{222}	−8.63	−8.46	−8.64
c_{123}	0.05	−0.33	−0.76
c_{144}	0.03	−0.37	−0.30
c_{155}	−1.02	−0.62	−0.58
c_{344}	−1.90	−1.90	−1.93

[a]Reference 22.

TABLE V. Contributions to the Fuchs elastic constants of Mg. The constants involving the volume-dependent energy term are not included here. Entries are in units of 10^{12} dyn cm^{-2}.

	Electrostatic contribution	Band-structure contribution	Internal-strain contribution	Calc. value	Expt. value[a]
$\frac{\partial^2 E}{\partial \epsilon^2}$	1.306	−0.505	···	0.801	0.728
$\frac{\partial^2 E}{\partial e^2}$	0.303	−0.059	−0.035	0.209	0.202
$\frac{\partial^2 E}{\partial \gamma^2}$	0.170	0.016	···	0.186	0.198
$\frac{\partial^2 E}{\partial \epsilon\, \partial v}$	0.001	−0.010	···	−0.009	−0.002
$\frac{\partial^3 E}{\partial \epsilon^3}$	3.10	−3.39	···	−0.29	−2.90
$\frac{\partial^3 E}{\partial e^3}$	0.36	−0.43	0.32	0.25	0.40
$\frac{\partial^3 E}{\partial \epsilon\, \partial v^2}$	−0.00	0.03	···	0.03	0.01
$\frac{\partial^3 E}{\partial v\, \partial \epsilon^2}$	−0.44	−1.51	···	−1.95	−1.73
$\frac{\partial^3 E}{\partial v\, \partial \gamma^2}$	−0.06	−0.38	···	−0.44	−0.29
$\frac{\partial^3 E}{\partial \epsilon\, \partial \gamma^2}$	−0.84	0.15	···	−0.69	−0.81
$\frac{\partial^3 E}{\partial e\, \partial \gamma^2}$	−0.11	0.45	−0.40	−0.06	−0.06
$\frac{\partial^3 E}{\partial v\, \partial e^2}$	−0.10	−0.49	0.17	−0.42	−0.32
$\frac{\partial^3 E}{\partial \epsilon\, \partial e^2}$	0.32	0.77	0.33	1.42	1.60

[a] Reference 22.

from an optimized model potential with corrections for exchange and correlation. The results of King and Culter are obtained from a first-principles nonlocal pseudopotential. The experimental values listed are the linearly extrapolated values at 0 °K; they are not the measured values at 0 °K, since the calculations have not included zero-point effects. It can be seen that the Ashcroft potential gives as good agreement with experiment as do more sophisticated potentials. Our value for the internal-strain parameter is in excellent agreement with that found by Cousins (Table VII).

TABLE VI. The second-order Brugger elastic constants and their pressure derivatives. These values were obtained by using the experimental value of $\partial^2 E/\partial v^2$. The elastic constants are in units of 10^{12} dyn cm^{-2}, and the pressure derivatives are dimensionless.

	Calc. value	Expt. value[a]
c_{11}	0.686	0.666
c_{12}	0.268	0.262
c_{13}	0.201	0.219
c_{44}	0.186	0.198
c_{33}	0.726	0.702
$c_{66}=\frac{1}{2}(c_{11}-c_{12})$	0.209	0.202
dc_{44}/dP	1.40	1.60
dc_{66}/dP	1.36	1.37
dc_{11}/dP	5.19	6.23
dc_{33}/dP	5.89	7.29

[a] Reference 22.

TABLE VII. Second-order shear constants of magnesium at 0 °K. Entries are in units of 10^{12} dyn cm^{-2}, and A is in units of the lattice parameter a.

Constant	This paper	Cousins	King and Cutler	Expt.
$\partial^2 E/\partial \epsilon^2$	0.801	0.768	0.609	0.728
$\partial^2 E/\partial e^2$	0.209	0.199	0.207	0.202
$\partial^2 E/\partial \gamma^2$	0.186	0.193	0.179	0.198
A	0.350	0.350	···	···

IV. SUMMARY AND CONCLUSIONS

A pseudopotential model was used to calculate the elastic constants of magnesium. The only adjustable parameters were the core radius r_c and the shear-independent term α. The equilibrium c/a ratio was calculated and found to be very close to the experimental value, and the internal-strain parameter was calculated by requiring the energy density of the strained state to be a minimum.

It was found that the energy density did not satisfy the equilibrium condition $\partial E/\partial v = 0$ at the observed atomic volume. To satisfy this condition, it was necessary to adjust the volume-dependent energy term. Specifically, the parameter α, which arises from first-order perturbation theory, was adjusted to obtain equilibrium.

Fuchs-type strain parameters were employed in calculating the elastic constants. The results are found to be rather insensitive to whichever dielectric function (Hartree or modified) is used. The calculated elastic constants are found to be in best agreement with experiment for $r_c = 1.358a_0$ (and the modified dielectric function), but there is only a slight preference over $r_c = 1.38a_0$ (and the Hartree dielectric function). It was found that internal-strain contributions to the Brugger elastic constants, although small, did improve the over-all agreement of theory with experiment.

The band-structure energy was found to contribute significantly to the elastic constants of magnesium, for which $Z = 2$. It was noticed, however, that band-structure effects had been small for the alkali metals ($Z = 1$), but large for aluminum ($Z = 3$). The agreement with experiment is excellent for $Z = 1$, good for $Z = 2$, and fair for $Z = 3$.

The core radius determined from elastic-constant calculations is in good agreement with the value obtained from calculations of electronic properties, such as the resistivity of liquid magnesium. That the same pseudopotential is successful in predicting both mechanical and electronic properties may give one confidence for its use in other calculations. The agreement with experiment of the calculated elastic constants is found to be good. This comparison is a detailed one, since elastic constants give changes of the energy density not only with respect to volume changes but also with respect to various shear deformations. This suggests that the interatomic potential may be known well enough to calculate properties of imperfect crystals. Both structural and thermal (phonon) defects are known to be predominantly shear in character.[23]

The results of this work represent the most accurate agreement to date between theory and experiment for the third-order elastic constants of a metal. The results are also in good agreement with calculations by Cousins and by King and Cutler, who used more sophisticated pseudopotentials, but calculated only the three second-order shear elastic constants. The only other metal for which a comparison of the complete set of third-order elastic constants has been made is aluminum, and there the agreement of theory with experiment is only fair. Better agreement has been obtained for the alkali metals, but the experimental data there is not sufficient to allow one to make a comparison for the complete set of third-order constants.

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