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THE SECOND AND THIRD ORDER ELASTIC CONSTANTS OF MAGNESIUM

EDWIN ROLAND NAIMON

Department of Physics and Materials Research Laboratory
University of Illinois, Urbana, Illinois
September, 1970

This is a technical information document based on a thesis submitted by Edwin Roland Naimon in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate College of the University of Illinois, 1970. The research was supported by the U.S. Atomic Energy Commission under Contract AT(11-1)-1198.

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THE SECOND AND THIRD ORDER ELASTIC CONSTANTS OF MAGNESIUM

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University of Illinois at Urbana-Champaign, 1970

(The complete set of the ten third order elastic constants of magnesium has been determined experimentally from measurements of the hydrostatic pressure and uniaxial compression derivatives of the natural sound velocities using an ultrasonic pulse superposition technique. The specimen was neutron irradiated to suppress dislocation effects.

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 cubic metals. The only adjustable parameter was the core radius r_c .

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 has proved successful in predicting both mechanical and electronic properties of magnesium.

Because magnesium exists in the non-primitive hexagonal close-packed 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 were small; the inclusion of internal strain, however, was found to improve the overall agreement between theory and experiment.

The calculated third order elastic constants of magnesium, obtained from using $r_c = 1.358 a_0$ and a modified dielectric function, are presented below, along with the experimentally determined values; the elastic constants here are in units of 10^{12} dynes cm^{-2} .

	<u>Theory</u>	<u>Experiment</u>
c_{111}	-6.71	-6.63
c_{112}	-1.69	-1.78
c_{113}	0.51	0.30
c_{222}	-8.46	-8.64
c_{123}	-0.33	-0.76
c_{133}	-1.11	-0.86
c_{333}	-6.32	-7.26
c_{144}	-0.37	-0.30
c_{155}	-0.62	-0.58
c_{344}	-1.90	-1.93

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I. INTRODUCTION

It is the purpose of this thesis to measure and calculate the second and third order elastic constants of magnesium. Many properties of solids can be described in terms of elastic constants. For example, the Debye temperature and the compressibility may be found from second order (or ordinary) elastic constants, and the Gruneisen constant can be expressed in terms of third order constants. Elastic constants are also of importance in describing defects and defect interactions in crystals. Since elastic constants are related to derivatives of the interatomic potentials, they are useful in determining the nature of binding forces. Elastic constants give changes of the energy density not only with respect to volume changes, but also with respect to shears. Thus much can be learned about interatomic potentials from the elastic constants. For metals a complete set of elastic constants should provide insight into the theory of metallic binding. Elastic constants generally can be measured to a greater degree of accuracy than can be obtained from theoretical calculations. Since approximations must be made in theoretical models, the elastic constants can serve as a useful guide in developing the theory.

Recently Suzuki, et al. have used a pseudopotential method to calculate the elastic constants of the alkali metals¹ (monovalent) and of aluminum² (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; this metal is simple in that 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 hexagonal close-packed (h.c.p.) structure, which has a basis of two atoms. The atoms in a h.c.p. structure are not at centers of symmetry; therefore elastic deformations will in general induce internal⁴ strains since the structure is non-primitive. 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 $(\frac{\partial E}{\partial w})_{\eta} = 0$.

In addition to the concept of internal strain, the structure of magnesium introduces another parameter, namely the c/a ratio. Suzuki's method can be used to calculate the equilibrium value of c/a , and a comparison with experiment may be performed.

Because of the valence and structure of magnesium, a comparison of the calculated values with those obtained from experiment should prove useful in the theory of metals.

The second order elastic constants of magnesium have been determined experimentally.⁵⁻⁷ In addition, the hydrostatic pressure derivatives of the second order constants have been reported.⁸ This information, however, is not sufficient to determine the complete set of third order constants. There are five second order and ten⁹ third order constants for crystals having the h.c.p. structure. Thus the hydrostatic pressure derivatives of the second order constants give only five experimental numbers which are related to the ten third order elastic constants. The experimental part of this thesis is concerned with measurements to determine the complete set of third order elastic constants of magnesium.

At the time this work was begun, there had been no third order constants reported for any h.c.p. metal. Recently, however, Swartz and Elbaum¹⁰ have measured the complete set of third order elastic constants of zinc; they did not present any theory to account for their results. Thus magnesium will be the first h.c.p. metal for which the experimental third order elastic constants can be compared directly with theory. The hydrostatic pressure derivatives of the second order constants of the h.c.p. metals Be,¹¹ Cd¹² and Zr¹³ have also been reported; as mentioned above, this information is insufficient to determine a complete set of third order constants. All these results were obtained by applying pressures of several kilobars, which gave readily measurable changes in the second order constants; it was necessary to correct for length changes due to increasing pressure in those experiments.

The additional information needed to experimentally determine a complete set of third order elastic constants can be obtained by measuring

the change of the second order constants when only one crystalline axis is stressed at a time. Since second order elastic constants are determined from measurements of the velocity of sound in a crystal, the third order constants are then simply related to the change in sound velocity due to an applied homogeneous stress, such as hydrostatic pressure or uniaxial compression.

Unfortunately, uniaxial compression of metal crystals is likely to introduce dislocation motion, and it is well known that dislocations affect the measured sound velocity. It is possible to pin down existing dislocations by neutron irradiating the metal sample. The stress level must then be kept low enough to prevent breakaway of dislocations from the pinning points. Stresses on the order of 10 bars appear to be sufficiently low to suppress dislocation effects. With such low stresses, the typical sound velocity changes are 10-100 parts per million. Detection of such small velocity changes requires an extremely sensitive electronic system.

A system capable of measuring relative velocity changes as small as 10^{-8} has recently been developed by Holder.¹⁴ The method is an improvement upon the pulse superposition technique of McSkimin,^{15,16} in which a phase coherent superposition of echoes is attained by varying the pulse repetition rate. The measured sound velocity is then directly related to the repetition rate. Holder's method, in addition to its greater sensitivity, has an advantage in that it automatically records the results.

In Holder's system, a gated carrier method is used to provide the pulses; the carrier signal is generated by a frequency synthesizer. By use of a frequency divider, the pulse repetition rate is always an integral number

of cycles of the carrier frequency. The round trip transit time t of a sound wave in a crystal is then simply proportional to $1/f$, f being the carrier frequency. When the crystal is stressed, the carrier frequency must be readjusted to maintain superposition; this change in frequency is directly related to the change in transit time or velocity.

The relationships between the third order elastic constants and the stress derivatives of the sound velocities have been summarized by Thurston and Brugger.¹⁷ They defined a "natural velocity," $w = 2L_o/t$, where L_o is the unstressed path length. The pressure derivative $\frac{\partial}{\partial P}(\rho_o w^2)_{T,P=0}$ was then expressed in terms of second and third order elastic constants for the various sound modes and applied stresses P ; ρ_o is the density of the unstressed material. It is easily shown that $\frac{\partial}{\partial P}(\rho_o w^2)_{T,P=0} = 2c \left(\frac{1}{w} \frac{\partial w}{\partial P} \right)_{T,P=0} = -2c \left(\frac{1}{t} \frac{\partial t}{\partial P} \right)_{T,P=0} = 2c \left(\frac{1}{f} \frac{\partial f}{\partial P} \right)_{T,P=0}$, where $c = (\rho_o w^2)_{T,P=0}$. Thus it is necessary to only measure the frequency changes due to applied stress; changes in path length need not be considered here.

The second section of this thesis will be concerned with the experimental determination of the complete set of ten third order elastic constants of magnesium. A calculation of the elastic constants will be presented in the third section, and conclusions will be discussed in the fourth section.

II. EXPERIMENTAL METHODS AND RESULTS

The single crystal of magnesium used throughout the experiment was obtained from Semi-Elements Inc., Saxonburg, Pennsylvania. The dimensions of the sample were approximately 18x19x20mm. The crystal was oriented with faces perpendicular to the $[\bar{1}2\bar{1}0]$, $[10\bar{1}0]$ and $[0001]$ directions, hereafter referred to as the a, b and c axes, respectively. Laue back reflection photographs showed the orientations to be better than 1° . A spectral analysis was provided with the sample, showing a composition of 99.95+% pure magnesium.

The crystal was polished until opposite faces were flat and parallel to 200 parts per million. Rough polishing was done on 3/0 emery paper saturated in kerosene. Finer polishing was done with various grades of aluminum oxide powder and oil, starting with 9.5 micron powder and ending with 1.0 micron powder. The dimensions were checked with a Brown and Sharpe electronic micrometer, which gives relative readings directly in microinches.

The second order elastic constants were measured by the pulse-echo-overlap method of Papadakis¹⁸ (a diagram of the setup is shown in Fig. 1); 10 MHz quartz transducers were attached to the crystal with phenyl salicylate (salol). Pulses of approximately 3 microsecond duration were supplied by an Arenberg PG-650C pulsed oscillator. A Matec attenuation recorder was used to intensify a pair of successive echoes on a cathode-ray oscilloscope tube; the other echoes were suppressed. The oscilloscope was triggered externally with a frequency synthesizer so that a cycle-for-cycle match of the two intensified echoes could be achieved. When the echoes are properly matched, the round trip transit time is the reciprocal of the triggering frequency. The transit times could be obtained to better than 2 nanoseconds. By attaching a dummy

Fig. 1. Block diagram of the Papadakis visual-overlap system.

transducer to the far end of the specimen, a transit time correction of 100 nsec/echo was determined for both longitudinal and shear waves. For purposes of comparison with the results of other investigators, a density of 1.738 gm.cm^{-3} was used. This made it possible to use the tabulated data of Eros and Smith⁵ directly.

The constants c_{11} and c_{33} were determined from the propagation of longitudinal waves in the basal plane and along the c axis, respectively. The constant $c_{66} = (c_{11} - c_{12})/2$ was found from a shear wave propagated along the a (or b) axis and polarized along the b (or a) axis. The constant c_{44} was determined from the shear wave propagated along the c axis, and from the shear wave propagated along the a or b axis and polarized along the c axis. We were not able to determine the constant c_{13} due to the orientation of our crystal. We could only propagate waves parallel and perpendicular to the c axis, and c_{13} can only be found by propagation at some other angle to the c axis. Throughout our work we will use the experimental value of c_{13} determined by Eros and Smith.

Our results for the adiabatic second order elastic constants are presented in Table 1 and compared with the values found by other investigators. Our results in every case fall within the range of their values. The errors presented are estimated from the uncertainties in the measured transit times and lengths.

After obtaining the second order elastic constants, the magnesium crystal was neutron irradiated to suppress dislocation effects. The irradiation was performed at the reactor lab of the University of Illinois; the integrated exposure was approximately 2×10^{18} (fast) neutrons/cm².

Table 1. The adiabatic second order elastic constants of Mg at 25°C. The results of the other investigators were normalized to a density of 1.738 gm cm^{-3} by Eros and Smith.⁵ Entries are in units of $10^{12} \text{ dynes cm}^{-2}$.

<u>c</u>	<u>This Experiment</u>	<u>Eros and Smith⁵</u>	<u>Long and Smith⁶</u>	<u>Slutsky and Garland⁷</u>
c_{11}	.5918±.0008	.5928	.5969	.5905
c_{33}	.6147±.0007	.6135	.616	.6125
$c_{66}=(c_{11}-c_{12})/2$	.1675±.0002	.1669	.1674	.1680
c_{44}	.1634±.0006	.1632	.1638	.1632
c_{13}	- - -	.2157	.217	.2130
c_{12}	.2568±.0009	.2590	.2622	.2545

We have used a modification of the McSkimin^{15,16} pulse superposition method to measure the stress derivatives of the natural sound velocities. The system is the same as that described by Holder.¹⁴ A block diagram of the setup is presented in Fig. 2. Holder's velocity system, in addition to its greater sensitivity, automatically records the results.

When measuring small velocity changes, it is extremely important to monitor the temperature of the specimen. A stress of one bar typically produces a relative velocity change of only several parts per million. A temperature change of only .01°C will produce a velocity change of the same order of magnitude. Before doing the stress experiments, we measured the temperature derivatives of the natural sound velocities. Then, for the stress

Fig. 2. Block diagram of the pulse superposition system.

experiments, we were able to normalize all the velocities to a standard temperature (22.000°C). The temperature was measured with chromel-advance thermocouples. A Honeywell 2768 microvolt potentiometer was used to measure the emf, and the unbalanced potential was fed into a Leeds and Northrup dc amplifier and Mosely 7100B strip-chart recorder. Full scale was set at 10 microvolts, so that the temperature could be read to a millidegree.

The temperature derivatives were determined over the range 5°C to 15°C. For these experiments the temperature was controlled by placing the specimen in a furnace which was surrounded by an ice bath. The temperature could be changed by adjusting the furnace coil current. The temperature derivatives of the natural sound velocities are presented in Table 2. The indicated errors represent the range of several measurements for each mode.

Using the relations $c = \rho v^2$ and $v = \frac{2L}{t} = \frac{2L_0}{t} \frac{L}{L_0} = w \frac{L}{L_0}$, it is easily shown that

$$\frac{1}{c} \left. \frac{\partial c}{\partial T} \right|_P = -\beta + 2 \alpha_L + 2 \frac{1}{w} \left. \frac{\partial w}{\partial T} \right|_P. \quad (1)$$

Here β is the volume thermal expansion coefficient and α_L is the coefficient of linear thermal expansion of the propagation axis. For magnesium, $\alpha_{\parallel \text{ to } c} = .265$, $\alpha_{\perp \text{ to } c} = .251$ and $\beta = 2\alpha_{\perp} + \alpha_{\parallel} = .767^{19}$ in units of $10^{-4} \text{ } ^\circ\text{C}^{-1}$. We have calculated $\frac{1}{c} \left. \frac{\partial c}{\partial T} \right|_P$ for the different modes and, in Table 3, compared our values with those of Slutsky and Garland.⁷ Their results are in tabular form, and we have calculated the derivatives from their room temperature values. Our values are expected to be more accurate since we measured the velocities at ten points over a 10° interval, whereas Slutsky and Garland

Table 2. The temperature derivatives of the natural velocities of Mg. Entries are in units of $10^{-4}^{\circ}\text{C}^{-1}$.

<u>Sound Mode</u>	<u>$\frac{1}{w} \frac{\partial w}{\partial T} \bigg _P$</u>
c_{11}	$-1.467 \pm .012$
c_{33}	$-1.49 \pm .01$
$c_{66} = \frac{1}{2}(c_{11} - c_{12})$	$-2.43 \pm .02$
c_{44} (along c axis)	$-2.38 \pm .01$
c_{44} (basal plane)	$-2.375 \pm .010$

Table 3. The logarithmic temperature derivatives of the second order elastic constants of Mg. Entries are in units of $10^{-4}^{\circ}\text{C}^{-1}$.

<u>c</u>	<u>$\frac{1}{c} \frac{\partial c}{\partial T} \bigg _P$</u>	<u>Slutsky and Garland⁷</u>
c_{11}	$-3.20 \pm .02$	-2.86
c_{33}	$-3.22 \pm .02$	-3.25
c_{66}	$-5.12 \pm .05$	-4.44
c_{44}	$-5.01 \pm .02$	-5.79

give only two points over a 20° interval. In addition they used the pulse-echo technique which is much less sensitive than a pulse superposition method.

We then proceeded to measure the hydrostatic pressure and uniaxial stress derivatives of the natural sound velocities. Hydrostatic pressure was obtained from a nitrogen gas tank and was measured by a Heise bourdon gauge. The pressure vessel contained a heater coil to keep temperature corrections to a minimum. The stress range for hydrostatic experiments was approximately $0-80 \text{ kg cm}^{-2}$. A Tinius Olsen universal testing machine, accurate to better than 1%, was used to apply uniaxial compression. The crystal was placed between indium shims when stressed, and the stress was applied through a ball joint to promote uniform compression. Here the stress range was kept below 20 kg cm^{-2} , except for the c_{44} modes, for which the stress never exceeded 6 kg cm^{-2} .

For a h.c.p crystal oriented with faces perpendicular to the a, b and c axes, there are four hydrostatic and ten uniaxial experiments to determine the ten third order elastic constants. These experiments are listed in Table 4. For each experiment the directly measured quantity is the change in carrier frequency f with applied stress P ; this change was always found to be linear. From a least squares fit of the data, we obtained $\left. \frac{1}{f} \frac{\partial f}{\partial P} \right|_{T,P=0}$ for each experiment; this quantity, however, is identically equal to $\left. \frac{1}{w} \frac{\partial w}{\partial P} \right|_{T,P=0}$, w being the natural sound velocity. It is easily shown that

$$\left. \frac{\partial}{\partial P} (\rho_0 w^2) \right|_{T,P=0} = 2 c \left. \frac{1}{w} \frac{\partial w}{\partial P} \right|_{T,P=0} , \quad (2)$$

Table 4. The sound velocity stress experiments.

<u>Expt. No.</u>	<u>Propagation axis</u>	<u>Polarization axis</u>	<u>Stress axis</u>	<u>$c = (\rho_0 w^2)_{P=0}$</u>
1	c	b	hydro.	c_{44}
2	b	a	hydro.	c_{66}
3	b	b	hydro.	c_{11}
4	c	c	hydro.	c_{33}
5	c	c	b	c_{33}
6	b	b	c	c_{11}
7	b	b	a	c_{11}
8	a	a	b	c_{11}
9	b	a	c	c_{66}
10	b	a	a	c_{66}
11	a	b	b	c_{66}
12	b	c	c	c_{44}
13	b	c	a	c_{44}
14	c	b	b	c_{44}

$$a = [1\bar{2}10], \quad b = [10\bar{1}0], \quad c = [0001]$$

where $c = (\rho_o w^2)_{T,P=0}$ is the appropriate second order elastic constant. The relations between the measured quantities $\frac{\partial}{\partial P}(\rho_o w^2)_{T,P=0}$ and the second and third order elastic constants have been found by Thurston and Brugger¹⁷ and are summarized in Table 5.

The coefficients s_{ij} of the elastic constants in Table 5 are the isothermal elastic compliances. They are related thermodynamically to the adiabatic compliances which, in turn, are related to the adiabatic second order elastic constants. The explicit relations are²⁰

$$s_{11}^S = \frac{c_{11}c_{33} - c_{13}^2}{(c_{11} - c_{12})\tilde{c}}, \quad (3)$$

$$s_{12}^S = \frac{c_{13}^2 - c_{12}c_{33}}{(c_{11} - c_{12})\tilde{c}},$$

$$s_{13}^S = \frac{-c_{13}}{\tilde{c}},$$

and
$$s_{33}^S = \frac{c_{11} + c_{12}}{\tilde{c}},$$

where $\tilde{c} = c_{33}(c_{11} + c_{12}) - 2c_{13}^2$. The c_{ij} are the adiabatic second order elastic constants of Table 1. The isothermal compliances s_{ij}^T are found from the adiabatic compliances s_{ij}^S through the relation²⁰

$$s_{ij}^T = s_{ij}^S + \frac{T \alpha_i \alpha_j}{\rho_o c_p}. \quad (4)$$

Here T is the absolute temperature, α_i and α_j are the linear thermal expansion coefficients, and c_p is the specific heat at constant pressure (.245 cal/gm⁻¹°C⁻¹ for Mg).¹⁹ The values of the isothermal compliances of Mg are given in Table 5.

Table 5. Relationships between the sound velocity stress derivatives and the elastic constants.

Expt. No.	$-\frac{\partial}{\partial P}(\rho_0 w^2)_{T,P=0}$
1	$2c_{44}K_1 + K_1(c_{144}+c_{155}) + K_3c_{344} + 1$
2	$2c_{66}K_1 + \frac{1}{2}K_1(c_{222}-c_{112}) + \frac{1}{2}K_3(c_{113}-c_{123}) + 1$
3	$2c_{11}K_1 + K_1(c_{111}+c_{112}) + K_3c_{113} + 1$
4	$2c_{33}K_3 + 2K_1c_{133} + K_3c_{333} + 1$
5	$2c_{33}s_{13} + (s_{11}+s_{12})c_{133} + s_{13}c_{333}$
6	$2c_{11}s_{13} + s_{13}(c_{111}+c_{112}) + s_{33}c_{113}$
7	$2c_{11}s_{12} + s_{12}c_{111} + s_{11}c_{112} + s_{13}c_{113}$
8	$2c_{11}s_{12} + s_{11}(c_{111}+c_{112}) + (s_{12}-s_{11})c_{222} + s_{13}c_{113}$
9	$2c_{66}s_{13} + \frac{1}{2}s_{13}(c_{222}-c_{112}) + \frac{1}{2}s_{33}(c_{113}-c_{123})$
10	$2c_{66}s_{11} + \frac{1}{2}(s_{11}-s_{12})c_{111} - \frac{1}{4}(s_{11}+s_{12})c_{112} + \frac{1}{4}(3s_{12}-s_{11})c_{222} + \frac{1}{2}s_{13}(c_{113}-c_{123})$
11	$2c_{66}s_{11} - \frac{1}{2}(s_{11}-s_{12})c_{111} - \frac{1}{4}(s_{11}+s_{12})c_{112} + \frac{1}{4}(3s_{11}-s_{12})c_{222} + \frac{1}{2}s_{13}(c_{113}-c_{123})$
12	$2c_{44}s_{33} + s_{13}(c_{144}+c_{155}) + s_{33}c_{344}$
13	$2c_{44}s_{13} + s_{11}c_{144} + s_{12}c_{155} + s_{13}c_{344}$
14	$2c_{44}s_{11} + s_{12}c_{144} + s_{11}c_{155} + s_{13}c_{344}$

$$s_{11} = s_{11}^T = 2.220 \times 10^{-12} \text{ cm}^2 \text{ dyn.}^{-1}$$

$$s_{33} = s_{33}^T = 1.992 \times 10^{-12} \text{ cm}^2 \text{ dyn.}^{-1}$$

$$s_{12} = s_{12}^T = -0.765 \times 10^{-12} \text{ cm}^2 \text{ dyn.}^{-1}$$

$$s_{13} = s_{13}^T = -0.493 \times 10^{-12} \text{ cm}^2 \text{ dyn.}^{-1}$$

$$K_1 = s_{11}^T + s_{12}^T + s_{13}^T = 0.962 \times 10^{-12} \text{ cm}^2 \text{ dyn.}^{-1}$$

$$K_3 = s_{33}^T + 2s_{13}^T = 1.006 \times 10^{-12} \text{ cm}^2 \text{ dyn.}^{-1}$$

The hydrostatic pressure derivatives of the natural sound velocities were measured first, expts. 1-4 of Tables 4 and 5. The velocity change for a typical hydrostatic experiment is shown in Fig. 3. From the measured quantities $\frac{\partial}{\partial P}(\rho_0 v^2)_{T,P=0}$, we calculated the hydrostatic pressure derivatives of the second order elastic constants, $c = \rho v^2$. It is easily shown that

$$\left. \frac{\partial c}{\partial P} \right|_{T,P=0} = \left. \frac{\partial}{\partial P}(\rho_0 v^2) \right|_{T,P=0} + c(K - 2K_L), \quad (5)$$

where $K = -\frac{1}{V} \left. \frac{\partial V}{\partial P} \right|_T$ and $K_L = -\frac{1}{L} \left. \frac{\partial L}{\partial P} \right|_T$ are the isothermal volume and linear compressibilities, respectively; the compressibilities are given in Table 5. The pressure derivatives of the elastic constants are compared in Table 6 to the values found by Schmunk and Smith.⁸ The error indicated with our results represents the range of several measurements. It should be noted here that very good agreement exists despite the difference in the pressure ranges; our experiments never exceeded 80 bars, whereas Schmunk and Smith worked in the kilobar region. Similar type comparisons have not been as good for the metals Cu, Ag,²¹ Au, and Al,³ for which a two crystal interferometric technique was used. We suspect that the thermal lags present in the two crystal method account for part of the previous disagreement with the results of investigators working at higher pressures.

We then performed the uniaxial experiments involving the c_{33} , c_{11} and c_{66} modes, expts. 5-11 of Tables 4 and 5. A typical natural velocity change for a uniaxial compression experiment is shown in Fig. 4. For convenience only, all the experiments were begun with a stress applied; they could have been started with no stress. Before carrying out the experiments which

Fig. 3. Natural velocity change vs. hydrostatic pressure for a c_{33} mode (expt. 4 of Tables 4 and 5).

Table 6. The hydrostatic pressure derivatives of the second order elastic constants of Mg. The indicated errors represent the range of several measurements for each mode.

<u>c</u>	$\left. \frac{\partial}{\partial P}(c = \rho v^2) \right _{T, P=0}$	
	<u>This experiment</u>	<u>Schmunk and Smith</u> ⁸
c_{44}	$1.60 \pm .04$	1.58
c_{66}	$1.37 \pm .02$	1.36
c_{11}	$6.23 \pm .20$	6.13
c_{33}	$7.29 \pm .03$	7.22

involved c_{44} , expts. 12-14 of Tables 4 and 5, it was necessary to neutron irradiate the crystal once more; apparently the effects of the first irradiation had annealed out. This was not observable in the other experiments since they are not dislocation-sensitive. By a dislocation-sensitive experiment we mean one for which there is a component of shear stress in the slip plane. The primary slip plane of the h.c.p. structure is the basal plane. Since we always compressed either parallel or perpendicular to the basal plane, the uniaxial stresses have no shear components in the base. However, the c_{44} sound wave does have a shear stress component in the basal plane. This means that experiments 1 and 12-14 of Table 4 are dislocation-sensitive. That these modes were dislocation-sensitive was borne out by the high attenuation of the propagating wave. For the second irradiation, the integrated exposure again was approximately 2×10^{18} (fast) neutrons per cm^2 .

Fig. 4. Natural velocity change vs. applied uniaxial stress for a c_{33} mode (expt. 5 of Tables 4 and 5). The experiment was begun with a 3.90 kg/cm² stress applied to the specimen.

We then performed the remaining uniaxial compression experiments; the stress level was kept extremely low, never exceeding 6 kg cm^{-2} . The results of the c_{44} experiments are less accurate than those of the other experiments for two reasons: 1) the stress levels were much lower, resulting in smaller velocity changes, and 2) the ultrasonic attenuation was higher, resulting in a decrease in sensitivity. The natural velocity could only be determined to 2 parts in 10^6 , whereas a part in 10^7 was easily attainable for the other experiments. The natural velocity change for a typical c_{44} uniaxial compression experiment is shown in Fig. 5.

The results for all the hydrostatic and uniaxial experiments are summarized in Table 7. The errors indicated represent the range of the measured values.

Salama and Alers²² have suggested that agreement between hydrostatic and uniaxial data is a good indication that dislocation effects are not present. No dislocation motion should occur during hydrostatic pressure experiments, so a comparison of the two sets of data should show whether uniaxial compression has introduced dislocation effects. We were able to make three such comparisons. The third order constants c_{144} , c_{155} and c_{344} were determined from the uniaxial data of experiments 12-14; the combination $(c_{144} + c_{155} + \frac{K_3}{K_1} c_{344})$ was then calculated and compared to the value obtained from hydrostatic experiment no. 1. Then, from the uniaxial data of experiments 6-10, we determined the constants c_{111} , c_{112} , c_{113} , c_{222} and c_{123} ; the combinations $(c_{111} + c_{112} + \frac{K_3}{K_1} c_{113})$ and $(c_{222} - c_{112} + \frac{K_3}{K_1} (c_{113} - c_{123}))$ were calculated and compared to the values obtained from hydrostatic experiments no. 3 and no. 2, respectively. The comparisons are presented in Table 8.

Fig. 5. Natural velocity change vs. applied uniaxial stress for a c_{44} mode (expt. 13 of Tables 4 and 5). The experiment was begun with a 1.13 kg/cm^2 stress applied to the specimen.

Table 7. Experimental data and results for sound velocity stress derivatives. The errors indicated in columns 4 and 5 represent the range of the measured values.

Expt. No.	c (dyn.cm ⁻²)	$\frac{1}{w} \frac{\partial w}{\partial T} \Big _P$ (°C ⁻¹)	$\frac{1}{w} \frac{\partial w}{\partial P} \Big _T$ (dyn. ⁻¹ cm ²)	$\frac{\partial(\rho_0 w^2)}{\partial P} \Big _{T,P=0}$ (dimensionless)
1	.1634x10 ¹²	-2.38x10 ⁻⁴	4.44±.13x10 ⁻¹²	1.45±.04
2	.1675	-2.43	3.60±0.05	1.20±.02
3	.5918	-1.467	4.76±0.17	5.64±.20
4	.6147	-1.49	5.46±0.02	6.72±.03
5	.6147	-1.49	-1.40±0.15	-1.72±.18
6	.5918	-1.467	-3.50±0.06	-4.14±.07
7	.5918	-1.467	-0.19±0.02	-0.22±.02
8	.5918	-1.467	-5.00±0.03	-5.92±.03
9	.1675	-2.43	-6.92±0.21	-2.32±.07
10	.1675	-2.43	-2.58±0.02	-0.86±.01
11	.1675	-2.43	16.32±0.84	5.47±.28
12	.1634	-2.375	8.63±1.95	2.82±.64
13	.1634	-2.375	-1.54±0.36	-0.50±.12
14	.1634	-2.38	-1.65±0.44	-0.54±.14

Table 8. Comparison of hydrostatic and uniaxial data. Entries are in units of 10^{12} dynes cm^{-2} .

<u>Elastic constant</u>	<u>Hydrostatic</u>	<u>Uniaxial</u>
$c_{144} + c_{155} + \frac{K_3}{K_1} c_{344}$	$-2.87 \pm .04$	$-3.12 \pm .70$
$c_{111} + c_{112} + \frac{K_3}{K_1} c_{113}$	$-8.08 \pm .20$	$^* -8.47 \pm .80$
$c_{222} - c_{112} + \frac{K_3}{K_1} (c_{113} - c_{123})$	$-5.25 \pm .04$	$^* -6.17 \pm .60$

$$\frac{K_3}{K_1} = \frac{s_{33}^T + 2s_{13}^T}{s_{11}^T + s_{12}^T + s_{13}^T} = 1.0455$$

The errors in the hydrostatic results represent the range of several measurements for each mode. The errors in the uniaxial results represent our confidence in the values.

* These values were determined from experiments 6-10. Experiment no. 11 is 20% too high and is not included for comparison here; it is included, however, in the determination of the complete set of third order elastic constants.

Our agreement in Table 8 is sufficient to assume that dislocations have not contributed to the measured stress derivatives.

We should mention that expt. no. 11 was not included in calculating the values for Table 8. The results for this experiment are approximately 20% higher than those obtained from the other hydrostatic and uniaxial experiments, and thus were not included for the comparisons. We have no definite explanation for this disagreement. The results of expt. 11 are used, however, in the determination of the complete set of third order elastic constants. The inclusion of this experiment does not affect the values of the third order constants; it does, however, increase the resulting standard deviations.

The hydrostatic and uniaxial data were then combined to obtain the third order elastic constants. A least squares program was used to determine the "best" values. The constants c_{133} and c_{333} were determined from expts. 4 and 5; the constants c_{111} , c_{112} , c_{113} , c_{222} and c_{123} were determined from expts. 2, 3, and 6-11; and the constants c_{144} , c_{155} and c_{344} were determined from expts. 1 and 12-14. The only weighting done was for the c_{44} experiments, where we felt that the hydrostatic measurement (expt. 1) was three times more accurate than the uniaxial measurements (expts. 12-14). The complete set of third order elastic constants is presented in Table 9. The errors indicated are the standard deviations arising from the least squares analysis and represent the consistency of the measurements.

It is of interest to see if the Cauchy relations are satisfied for the elastic constants of magnesium. These are simple relations that can be derived when the interactions between atoms are due to central forces and when each atom is at a center of symmetry. The Cauchy relations for the

Table 9. The third order elastic constants of Mg at 22°C. The errors indicated are the standard deviations and represent the consistency of the measurements. Entries are in units of 10^{12} dynes cm^{-2} .

c_{133}	=	-0.86	±	.03
c_{333}	=	-7.26	±	.06
c_{111}	=	-6.63	±	.25
c_{112}	=	-1.78	±	.14
c_{113}	=	+0.30	±	.16
c_{222}	=	-8.64	±	.25
c_{123}	=	-0.76	±	.35
c_{144}	=	-0.30	±	.03
c_{155}	=	-0.58	±	.03
c_{344}	=	-1.93	±	.03

second order elastic constants are $c_{13} = c_{44}$ and $c_{12} = c_{66}$; the third order Cauchy relations are

$$\begin{aligned} c_{456} = c_{366} = c_{144} = c_{123}, \quad c_{166} = c_{112}, \\ c_{266} = c_{122}, \quad c_{155} = c_{113}, \text{ and } c_{344} = c_{133}. \end{aligned} \quad (6)$$

Many of these constants are not the tabulated values, but linear combinations of them. The relations⁹ and values are

$$\begin{aligned}
c_{166} &= \frac{1}{4} (3c_{222} - 2c_{111} - c_{112}) = -2.72, \\
c_{266} &= \frac{1}{4} (2c_{111} - c_{222} - c_{112}) = -0.71, \\
c_{366} &= \frac{1}{2} (c_{113} - c_{123}) = 0.53, \\
c_{456} &= \frac{1}{2} (c_{155} - c_{144}) = -0.14, \\
c_{122} &= c_{111} - c_{222} + c_{112} = 0.23
\end{aligned}$$

in units of 10^{12} dynes cm^{-2} .

From the above values and those of Tables 1 and 9, it can be seen that the Cauchy relations are not satisfied. There does not seem to be a trend toward the Cauchy relations becoming satisfied for higher order elastic constants. This is in contrast to the results obtained for the noble metals;²¹ there, however, the dominant contributions to the higher order constants were central-force-type interactions and the atoms were at centers of symmetry. We will see in the next section that the elastic constants of magnesium cannot be determined from a central-force model. In addition, since the atoms are not at centers of symmetry, the Cauchy relations are not expected to hold for magnesium.

III. CALCULATIONS OF THE ELASTIC CONSTANTS OF MG

Until now, there has not yet been a model which successfully predicts the second and third order elastic constants of magnesium. Huntington²³ has calculated the electrostatic contributions to the three second order elastic shear constants of Mg; the agreement with experiment was good for c_{44} , but poor for the other two shear constants. We will see later that the band structure energy obtained from pseudopotential theory does contribute significantly to the other two shear constants, and that it contributes little to c_{44} . Huntington has neglected internal strains, but it will be seen that this does not affect c_{44} .

Reitz and Smith²⁴ extended Huntington's calculations by considering the change in Fermi energy E_F caused by movements of the Brillouin zone planes as the metal is sheared. Their procedure is similar to Leigh's²⁵ method for calculating the shear constants of aluminum; Suzuki² has recently discussed the shortcomings of Leigh's calculations. The main point is that derivatives of E_F with respect to shear strains were calculated under the assumption that the change of E_F was due to the displacement of the energy gap at the Brillouin zone boundaries and to the accompanying redistribution of electrons within and between the zones; the energy versus momentum relationship on either side of the zone boundaries was assumed to remain the same during the deformation. Reitz and Smith, by introducing an effective valence Z_{eff} along with several other adjustable parameters, were able to obtain agreement with experiment for two shear constants; the constant c_{44} was not calculated because of a more complicated distortion of the Brillouin zones. The results of Reitz and Smith were then extended to calculations of the pressure derivatives of the second

order shear constants of Mg by Schmunk and Smith.⁸ By using the parameters of Reitz and Smith, they found the agreement with experiment to be poor. To obtain agreement, they found it necessary, as in the case of aluminum, to add an additional adjustable parameter, namely the pressure dependence of Z_{eff} , to the parameters already used in the second order elastic constant calculations. In the case of aluminum, Thomas³ tried to extend Leigh's method to the calculation of third order elastic constants; the method proved to be unsuccessful.

The above model has been referred to by Harrison²⁶ as a "rigid band structure model". He has commented that the most important aspect of the problem is the corresponding change in band structure as the lattice is deformed, and that the redistribution of electrons in a rigid band structure is quite unimportant. It should be noted that the relative number of electrons near a zone boundary is small, and it is expected that other regions of the zone contribute significantly to the elastic constants.

Slutsky and Garland^{7,27} used an entirely different approach to calculate the second order elastic constants of magnesium. Three parameters (force constants) entered from using a central-force model involving interactions between first, second, and third nearest neighbors. A fourth parameter was introduced to account for a volume-dependent energy term. The five second order elastic constants were then expressed in terms of the four parameters. The parameters were determined by fitting them to four of the five experimentally determined elastic constants. The fifth constant was then successfully predicted. This approach is of little interest for the present purposes.

More recently Cousins²⁸ calculated electrostatic and repulsive ion-ion contributions to the elastic shear constants of hexagonal metals for various

c/a ratios. Since there is very little core-overlap in magnesium, the repulsive ion-ion effects may be neglected here. Cousins's results are in exact agreement with our electrostatic calculations if a sign is changed in one of his results.²⁹

The above references have failed to give a model from which all the elastic constants and their pressure derivatives may be predicted. In addition, none of them have considered internal strain contributions to the elastic constants. In this section we will develop a simple method which successfully predicts the elastic properties of magnesium.

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

$$c_{ijklmn\dots} = \left(\frac{\partial^n E}{\partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}} \right)_{\eta=0} \quad (7)$$

The above elastic constant is of the type defined by Brugger.³⁰ 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 $J_{ik} = \frac{\partial x'_k}{\partial x_i}$ and δ_{ij} is the Kronecker delta. 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 Fuchs³¹ 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 later 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.

$$\begin{aligned}x'_1 &= (1+\epsilon)^{-1/2} x_1 \\x'_2 &= (1+\epsilon)^{-1/2} x_2 \\x'_3 &= (1+\epsilon) x_3\end{aligned}$$

x_1 , x_2 and x_3 are shown in Fig. 6; the prime refers to the strained state.

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.

Fig. 6. The coordinate system for the h.c.p. structure. $\vec{x}_3$ is parallel to the c axis, i.e., out of the paper. $\vec{\tau}$ may be written as $\vec{\tau} = \frac{2}{3} \vec{x}_1 + \frac{1}{2} \vec{x}_3$.

$$x'_1 = x_1$$

$$x'_2 = x_2 + \gamma x_3$$

$$x'_3 = x_3$$

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.

$$x'_1 = (1+e)^{1/2} x_1$$

$$x'_2 = (1+e)^{-1/2} x_2$$

$$x'_3 = x_3$$

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.

$$x'_1 = v^{1/3} x_1$$

$$x'_2 = v^{1/3} x_2$$

$$x'_3 = v^{1/3} x_3$$

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 We will give a brief description here.

With $J_{ij} = \frac{\partial x'_i}{\partial x_j}$, we easily find that for an ϵ strain the matrix J_{ij} is given by

$$J_{ij} = \begin{pmatrix} (1+\epsilon)^{-1/2} & 0 & 0 \\ 0 & (1+\epsilon)^{-1/2} & 0 \\ 0 & 0 & (1+\epsilon) \end{pmatrix}.$$

Since $\eta_{ij} = \frac{1}{2} (J_{ik} J_{jk} - \delta_{ij})$, we find the matrix η_{ij} to be

$$\eta_{ij} = \frac{1}{2} \begin{pmatrix} (1+\epsilon)^{-1} - 1 & 0 & 0 \\ 0 & (1+\epsilon)^{-1} - 1 & 0 \\ 0 & 0 & (1+\epsilon)^2 - 1 \end{pmatrix}.$$

By chain differentiation, we see that

$$\frac{\partial E}{\partial \epsilon} = \frac{\partial E}{\partial \eta_{ij}} \frac{\partial \eta_{ij}}{\partial \epsilon}, \quad \text{and}$$

$$\frac{\partial^2 E}{\partial \epsilon^2} = \frac{\partial E}{\partial \eta_{ij}} \frac{\partial^2 \eta_{ij}}{\partial \epsilon^2} + \frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \frac{\partial \eta_{ij}}{\partial \epsilon} \frac{\partial \eta_{kl}}{\partial \epsilon}.$$

The elastic constants are evaluated in the unstrained state. Thus $\left(\frac{\partial E}{\partial \eta_{ij}} \right)_0 = 0$ from equilibrium conditions, and $\left(\frac{\partial^2 E}{\partial \eta_{ij} \partial \eta_{kl}} \right)_0 = c_{ijkl}$. In the unstrained state,

$$\frac{\partial \eta_{ij}}{\partial \epsilon} = \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

$$\begin{aligned} \text{Then } \frac{\partial^2 E}{\partial \epsilon^2} = & c_{1111}(1/4) + c_{1122}(1/4) + c_{1133}(-1/2) \\ & + c_{2211}(1/4) + c_{2222}(1/4) + c_{2233}(-1/2) \\ & + c_{3311}(-1/2) + c_{3322}(-1/2) + c_{3333}(1) \end{aligned}$$

From here on, the Voight reduced notation will be used; $11 \rightarrow 1$, $22 \rightarrow 2$, $33 \rightarrow 3$, $23 \rightarrow 4$, $13 \rightarrow 5$, $12 \rightarrow 6$. Using the symmetry relations⁹ for h.c.p. crystals, we find that

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

The relationships between the Fuchs constants and Brugger constants for h.c.p. structures are summarized in Table 10.

Our choice of Fuchs constants is not unique, but represents all the independent second and third order elastic constants of a h.c.p. 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. Thus, in calculating $\partial^3 E / \partial \epsilon \partial \gamma^2$, the appropriate J matrix is $J = J_{\gamma} J_{\epsilon}$.

What is needed now to actually calculate the elastic constants is an expression for the energy density. We will first consider a jellium-type model. Here the metal is considered to be made up of positive point charges arranged on a lattice and embedded in a uniform sea of conduction electrons. The resulting Coulomb energy E_c is attractive. The repulsive part of the energy comes from the kinetic energy of the electron gas. We can then write the total

Table 10. Relationships between Fuchs and Brugger constants for h.c.p. crystals.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

energy as

$$E = E_c + \frac{3}{5} E_F, \quad (8)$$

where E_F is the Fermi energy. This jellium model is identical to that described by Kittel.³² It is not the jellium model considered, for example, by Ziman³³ or Pines;³⁴ there properties of an electron gas were being studied, and jellium was a uniform positively charged medium against which the electrons moved. The metal thus had no structure, and all shear elastic constants become identically zero. Kittel's model, on the other hand, does consider the lattice structure if treated properly. This is so because the Coulomb energy is dependent upon the structure of the positive-ion lattice.

Following Kittel, the Coulomb energy of our jellium model can be closely approximated by calculating the energy of an ion interacting electrostatically with an atomic sphere of uniform negative charge. The energy of jellium may then be written as

$$E = -1.8 \frac{Z^{2/3}}{r_s} + .6 k_F^2 \quad (9)$$

Here E is in units of Rydbergs per electron; Z is the valence; r_s is given by $\frac{4}{3} \pi r_s^3 = V_0/Z$, where V_0 is the atomic volume; k_F is the radius of the Fermi sphere and is given by $k_F^3 = 3\pi^2 Z/V_0$; k_F and r_s are measured in atomic units here. The coefficient -1.8 in Eq. 9 is an excellent approximation for h.c.p., b.c.c. and f.c.c. lattices.²⁶

The lattice parameter may be calculated by requiring that our jellium model be in equilibrium. This means that $\partial E / \partial v = 0$, where v is a previously

discussed Fuchs strain parameter. For this strain, $r'_s = v^{1/3} r_s$ and $k'_F = v^{-1/3} k_F$. We then find the equilibrium value of r_s to be $r_s = \frac{2.45}{Z^{2/3}}$. For magnesium, $Z = 2$; then $r_s = 1.54$, compared to an experimental value of 2.64.²⁶

Thus jellium fails to predict a good value for the atomic volume of magnesium.

Kittel calculated the bulk modulus of jellium using the energy density of Eq. 9.

However, he then calculated the velocity of a longitudinal sound wave by

equating this bulk modulus to the effective elastic constant. This would only

be valid for the Pines-type jellium model, for which the shear constants vanish.

Suzuki, et al.,¹ by taking into account the structure, have calculated both the longitudinal and shear elastic constants of the cubic jellium metals.

We have just seen that a reasonable lattice parameter cannot be obtained from jellium. We can, however, force our jellium model to be in equilibrium at the observed atomic volume by varying the volume-dependent energy term. Since E_F is proportional to $V_0^{-2/3}$, we may write the energy of jellium as

$$E = E_c + P v^{-2/3}, \quad (10)$$

where P is determined by requiring that $\partial E / \partial v = 0$ at the observed atomic volume; i.e., $-\frac{1}{3} E_c - \frac{2}{3} P = 0$. This is the jellium model discussed by Suzuki, et al.¹ The Coulomb energy is the same as that of Kittel, but the volume-dependent energy has been modified to provide equilibrium at the observed atomic volume.

As remarked earlier, the approximation of $E_c = -1.8 Z^{2/3} / r_s$ is an excellent one for h.c.p and other structures. In order to take derivatives of

E_c with respect to shear strains, however, it will be necessary to use an expression which explicitly contains the lattice structure. The Coulomb energy of a h.c.p. jellium metal, according to the Ewald-Fuchs³⁵ method, can be written as

$$E_c = \frac{Z^{2/3}}{r_s} \left(\frac{3}{4\pi} \right)^{1/3} \left[\begin{aligned} & \sum'_l \phi_{-1/2} \left(\frac{|\vec{R}_l|^2}{V_o^{2/3}} \pi \right) \\ & + \sum_l \phi_{-1/2} \left(\frac{|\vec{R}_l + \vec{\tau}|^2}{V_o^{2/3}} \pi \right) \\ & + \sum'_l \cos^2 \left(\frac{1}{2} \vec{q}_l \cdot \vec{\tau} \right) \phi_o \left(\frac{V_o^{2/3} q_l^2}{4\pi} \right) \end{aligned} \right] \quad (11)$$

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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. For an ideal c/a ratio, the coefficient of $Z^{2/3}/r_s$ is found to be -1.79168, which is very close to the value -1.8 found earlier. The energy expression for our jellium model is now complete; the Coulomb term E_c is given by Eq. 11, and the volume-dependent term is given by $Pv^{-2/3}$, with P determined by requiring that $\partial E/\partial v = 0$ at the observed atomic volume.

For h.c.p. metals another equilibrium condition must be satisfied, namely that $\frac{\partial E}{\partial (c/a)} = 0$. This is equivalent to having $\partial E/\partial \epsilon = 0$, where ϵ is a

previously discussed Fuchs strain. The $Pv^{-2/3}$ term does not enter here. One need only find the c/a ratio for which $\partial E_c / \partial \epsilon = 0$. By numerical methods, we have found $c/a = 1.6356$ to be the equilibrium value; the experimental value for Mg is 1.6228.³⁶

It is now easy to see one advantage of the Fuchs strains. The $Pv^{-2/3}$ term contributes to only two Fuchs constants, $\frac{\partial^2 E}{\partial v^2}$ and $\frac{\partial^3 E}{\partial v^3}$. It contributes nothing to the Fuchs constants which involve the shear strains ϵ , e or γ . On the other hand, the $Pv^{-2/3}$ term contributes to four second order and seven third order Brugger constants.

The derivatives of E_c with respect to the Fuchs strains are readily taken. Any lattice vector may be written as (see Fig. 6)

$$\vec{R}_\ell = \ell_1 \vec{x}_1 + \ell_2 \vec{x}_2 + \ell_3 \vec{x}_3,$$

where $\ell_1 + \ell_2 = \text{even integer}$ and $x_1 = \sqrt{3} a/2$, $x_2 = a/2$, and $x_3 = c$. Similarly, any reciprocal lattice vector may be expressed as

$$\vec{q}_\ell = \ell_1 \vec{G}_1 + \ell_2 \vec{G}_2 + \ell_3 \vec{G}_3,$$

with the same restriction on $\ell_1 + \ell_2$. Here $G_1 = \pi/x_1$, $G_2 = \pi/x_2$, and $G_3 = 2\pi/x_3$. For a given Fuchs strain, we know exactly how the lattice and reciprocal lattice vectors deform. For a v strain,

$$\vec{R}_\ell' = v^{1/3} \vec{R}_\ell,$$

$$\vec{q}_\ell' = v^{-1/3} \vec{q}_\ell,$$

and

$$V_o' = v V_o.$$

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

$$\vec{R}_\ell' = \ell_1(1+\epsilon)^{-1/2}\vec{x}_1 + \ell_2(1+\epsilon)^{-1/2}\vec{x}_2 + \ell_3(1+\epsilon)\vec{x}_3,$$

$$\vec{q}_\ell' = \ell_1(1+\epsilon)^{1/2}\vec{G}_1 + \ell_2(1+\epsilon)^{1/2}\vec{G}_2 + \ell_3(1+\epsilon)^{-1}\vec{G}_3,$$

$$\text{and } V_o' = V_o.$$

It is now that we come to an often neglected but very important point.

The hexagonal close-packed structure is non-primitive; it consists of two interpenetrating hexagonal sublattices that are separated by a vector $\vec{\tau}$. The position vectors of the two atoms in the ℓ^{th} unit cell are given by $\vec{R}_\ell$ and $\vec{R}_\ell + \vec{\tau}$. As seen above, we know how $\vec{R}_\ell$ deforms under a homogeneous deformation such as a Fuchs strain. We do not know, however, how the vector $\vec{\tau}$ will deform. If the components of $\vec{R}_\ell$ deform as

$$(\vec{R}_\ell')_i = J_{ik}(\vec{R}_\ell)_k,$$

then, for a general homogeneous deformation,⁴

$$(\vec{R}_\ell' + \vec{\tau}')_i = J_{ik}(\vec{R}_\ell + \vec{\tau})_k + (\vec{w})_i.$$

$\vec{w}$ 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 Kleinman³⁷ 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 tries 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 non-vanishing 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
$$\tau_1 = \frac{2}{3} x_1, \tau_2 = 0, \tau_3 = \frac{1}{2} x_3, \text{ and } \hat{x}_i = \frac{\vec{x}_i}{|\vec{x}_i|}.$$

Differentiations with respect to e are readily taken once w is known.

Obviously w is a function of e , so we may perform a power series expansion;

$$w = Ae + Be^2 + \dots \quad (12)$$

We will show 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

$$\frac{dE}{de} = \left(\frac{\partial E}{\partial e} \right)_w + \left(\frac{\partial E}{\partial w} \right)_e \frac{\partial w}{\partial e} = E_e + E_w w_e; \quad (13)$$

the subscripts refer to partial derivatives. We have stated earlier that w is determined by requiring the energy density of the strained state to be a minimum. This means that $E_w = \left(\frac{\partial E}{\partial w} \right)_e$ must be zero for all values of e .

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

$$\frac{d}{de} E_w \equiv 0 = E_{ew} + E_{ww} w_e. \quad (14)$$

Equation 14 is identically zero for all e . Since $(w_e)_{e=0} = A$, we find that

$$A = - \left(\frac{E_{ew}}{E_{ww}} \right)_{e=0}. \quad (15)$$

Differentiating Equation 13 with respect to e and setting $E_w = 0$, we obtain

$$\frac{d^2 E}{de^2} = E_{ee} + E_{ew} w_e. \quad (16)$$

Since the elastic constants are evaluated in the unstrained state,

$$\left(\frac{d^2 E}{de^2}\right)_0 = (E_{ee})_0 + A(E_{ew})_0 \quad (17)$$

The last term in Eq. 17 is the internal strain contribution to the Fuchs constant.

By differentiating equations 16 and 14 with respect to e , we obtain

$$\frac{d^3 E}{de^3} = E_{eee} + 2E_{eew} w_e + E_{eww} w_e^2 + E_{ew} w_{ee}, \quad (18)$$

and

$$0 = E_{eew} + 2E_{eww} w_e + E_{www} w_e^2 + E_{ww} w_{ee}. \quad (19)$$

Multiplying Eq. 19 by w_e and adding this to Eq. 18 gives

$$\begin{aligned} \frac{d^3 E}{de^3} &= E_{eee} + 3E_{eew} w_e + 3E_{eww} w_e^2 + E_{www} w_e^3 \\ &+ w_{ee} [w_e E_{ww} + E_{ew}] \end{aligned} \quad (20)$$

But the coefficient of w_{ee} is identically zero by Equation 14. Evaluating Eq. 20 in the unstrained state, we find that

$$\left(\frac{d^3 E}{de^3}\right)_0 = (E_{eee})_0 + 3A(E_{eew})_0 + 3A^2(E_{eww})_0 + A^3(E_{www})_0 \quad (21)$$

Equation 21 is exact; we see that only the linear term of Eq. 12 is needed. The other elastic constants involving e are $\frac{d^3 E}{dvde^2}$, $\frac{d^3 E}{d\epsilon de^2}$, and $\frac{d^3 E}{d\epsilon dy^2}$. It can easily be shown that

$$\left(\frac{d^3 E}{dvde^2}\right)_0 = (E_{vee})_0 + 2A(E_{vve})_0 + A^2(E_{vww})_0, \quad (22)$$

$$\left(\frac{d^3 E}{d\epsilon de^2}\right)_0 = (E_{eee})_0 + 2A(E_{\epsilon ve})_0 + A^2(E_{\epsilon ww})_0, \quad (23)$$

$$\text{and} \quad \left(\frac{d^3 E}{ded\gamma^2}\right)_0 = (E_{e\gamma\gamma})_0 + A(E_{w\gamma\gamma})_0. \quad (24)$$

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

There is one second order Fuchs constant ($d^2 E/de^2$) and four third order constants ($d^3 E/de^3$, $d^3 E/dvde^2$, $d^3 E/d\epsilon de^2$ and $d^3 E/ded\gamma^2$) 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. The Fuchs parameters thus have the advantage that they reduce the number of elastic constants for which internal strain contributions must be calculated.

In the jellium model the only term contributing to internal strain is the Coulomb energy E_c . For this model we have found that $A = .8575 a$. This is the same value Floyd and Kleinman³⁷ found if only their Coulomb energy is considered. The results of the jellium model are given in Table 11. The $A = 0$ quantities are given in parentheses when there is a difference; these correspond to values calculated by completely ignoring internal strain. In the table we have compared the second order Fuchs constants and the third order Brugger constants with the experimental³⁶ values. The agreement with experiment

Table 11. Elastic constant calculations using a jellium model. Entries are in units of 10^{12} dynes cm^{-2} . The values in parentheses are those calculated by neglecting internal strain, i.e., $A = 0$.

Elastic Constant	Calculated Value	Exp. value ³⁶
$\partial^2 E / \partial \epsilon^2 = \frac{1}{2} (c_{11} + c_{12} + 2c_{33} - 4c_{13})$	1.318	0.728
$\partial^2 E / \partial e^2 = \frac{1}{2} (c_{11} - c_{12}) = c_{66}$	0.115 (0.304)	0.202
$\partial^2 E / \partial v^2 = \frac{1}{9} (2c_{11} + 2c_{13} + 4c_{33} + c_{33})$	0.231	0.382
$\partial^2 E / \partial \gamma^2 = c_{44}$	0.168	0.198
$\partial^2 E / \partial \epsilon \partial v = \frac{1}{3} (c_{13} + c_{33} - c_{11} - c_{12})$	0.000	-0.002
c_{133}	-1.15	-0.86
c_{333}	-3.63	-7.26
c_{111}	-3.01 (-4.07)	-6.63
c_{112}	-2.78 (-1.85)	-1.78
c_{113}	1.49 (0.67)	0.30
c_{222}	-7.30 (-6.62)	-8.64
c_{123}	-0.49 (0.33)	-0.76
c_{144}	-0.78 (0.17)	-0.30
c_{155}	1.01 (0.06)	-0.58
c_{344}	-1.76	-1.93

can at best be described as fair, although the order of the larger constants is predicted very well (i.e., c_{222} is largest, etc.). It can be seen that internal strain contributions are significant; however, in this model the internal strain parameter is so large that the overall agreement is better if the internal strains are neglected. We will see later that internal strain

effects are really smaller, and that they do tend to improve the agreement with experiment. We should remember that our jellium model is an idealized metal; in addition, we had to modify the Fermi energy to guarantee equilibrium at the observed atomic volume. The jellium model has proved useful in illustrating the techniques used in the calculation of elastic constants; moreover, the agreement with experiment does indicate that one can hope for improvement by using a suitable perturbation method.

We will now derive a perturbation or band structure energy term by employing a pseudopotential theory; a more complete description may be found in the book by Harrison.²⁶ It will be seen that the band structure energy contributes very little to the binding energy; however, some of the strain derivatives of this energy term will not be small, and there will then be significant contributions to the elastic constants.

Before proceeding, we will make three fundamental, but important, approximations. The first is the one-electron approximation, namely that the real potential seen by an electron may be replaced by a self-consistent potential. The second approximation is that the ion cores are small; this allows us to separate the electron energy levels into core states and conduction-band states. Since the cores do not overlap, the only direct ion-ion interaction is Coulombic. We assume that the potential due to the conduction electrons and the other ions does not vary over an ion core; the wave functions of the core states are then the same as in the isolated ion. We thus know the core states, and we need only find the conduction-band states. Our third approximation is the Born-Oppenheimer approximation, namely that we assume that the electrons adiabatically follow the motion of the ions. This enables us to obtain an equation for a wave function of the electrons alone.

We may now write the Schrödinger equation for an electron in a metal as

$$H \psi_k = (T + V(\vec{r})) \psi_k = E_k \psi_k \quad (25)$$

Here $T = \frac{\hbar^2 \nabla^2}{2m}$, $V(\vec{r})$ is the self-consistent potential seen by each electron, and E_k is the energy of the k^{th} state.

A method of finding ψ_k is to expand it in a complete set of states and substitute into Eq. 25. One could use plane waves for the expansion, but a large number would be needed to describe ψ_k fairly well. Since the conduction-band states must be orthogonal to the core states, an expansion in plane waves already orthogonalized to the core states will be much more rapidly convergent. Such expansion terms are known as orthogonalized plane waves (OPW's). We will denote a plane wave by $|\vec{k}\rangle = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$; $|\alpha\rangle$ will designate a core state, and ψ_k will refer to a conduction-band state.

We then have

$$\text{OPW}_k \equiv |\vec{k}\rangle - \sum_{\alpha} |\alpha\rangle \langle \alpha | \vec{k} \rangle \quad (26)$$

Obviously, $\langle \alpha | \text{OPW}_k \rangle = 0$. ψ_k is now expanded in OPW's so that

$$\psi_k = \sum_q a_q(\vec{k}) \text{OPW}_{k+q} = \sum_q a_q(\vec{k}) \left[|\vec{k}+\vec{q}\rangle - \sum_{\alpha} |\alpha\rangle \langle \alpha | \vec{k}+\vec{q} \rangle \right] \quad (27)$$

By substituting ψ_k of Eq. 27 into Eq. 25, and with a rearrangement of terms, we may obtain an equation of the form

$$T \phi_k + W \phi_k = E_k \phi_k, \quad (28)$$

where

$$W = V(\vec{r}) + \sum_{\alpha} (E_k - E_{\alpha}) |\alpha\rangle \langle \alpha| \quad (29)$$

and

$$\phi_k = \sum_q a_q(\vec{k}) |\vec{k} + \vec{q}\rangle. \quad (30)$$

No approximations have been made; only a rearrangement of terms has occurred. W is known as the pseudopotential, and ϕ_k is the pseudo wave function. E_k is the energy eigenvalue corresponding to ϕ_k of Eq. 28 and ψ_k of Eq. 25.

Phillips and Kleinman⁴¹ have shown that the last term in Equation 29 tends to cancel the $V(\vec{r})$ term. Thus W is small in the core region and behaves like $V(\vec{r})$ outside the core. We will now solve Equation 28 by standard perturbation techniques, neglecting the potential altogether for the zero-order approximation. We then obtain, to second order,

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m} + \langle \vec{k} | W | \vec{k} \rangle + \sum_q \frac{\langle \vec{k} + \vec{q} | W | \vec{k} \rangle \langle \vec{k} | W | \vec{k} + \vec{q} \rangle}{\frac{\hbar^2}{2m} [k^2 - |\vec{k} + \vec{q}|^2]}. \quad (31)$$

If we assume that $W(\vec{r})$ may be written as a sum of potentials centered on the N ion positions $\vec{r}_i$, i.e.,

$$W(\vec{r}) = \sum_i^N w(|\vec{r} - \vec{r}_i|), \quad (32)$$

then it is easy to show that

$$\langle \vec{k} + \vec{q} | W(\vec{r}) | \vec{k} \rangle = S(\vec{q}) \langle \vec{k} + \vec{q} | w(r) | \vec{k} \rangle. \quad (33)$$

Here $S(\vec{q})$ is the structure factor, given by

$$S(\vec{q}) = \frac{1}{N} \sum_j e^{-i\vec{q} \cdot \vec{r}_j} \quad (34)$$

$S(\vec{q})$ depends only upon the ion positions. The structure factor here is the same as that used in x-ray and other diffraction theories. $\langle \vec{k} + \vec{q} | w(r) | \vec{k} \rangle$ is known as the form factor and is independent of the ion positions. The total energy of the electrons is obtained by summing Equation 31 over the occupied states. This means we include all $k < k_F$, where k_F is the radius of the Fermi sphere. The sum is converted to an integral by means of the density of states relation, $\sum_k = \frac{2V}{(2\pi)^3} \int d^3k$. Performing the sum and dividing by the number of electrons (NZ), we find the eigenvalue sum per electron E_{e1} to be

$$E_{e1} = \frac{3}{5} E_F + \overline{\langle \vec{k} | w | \vec{k} \rangle} + \sum_q S^*(\vec{q}) S(\vec{q}) \frac{2 V_0}{(2\pi)^3 Z} \int \frac{d^3k \langle \vec{k} | w | \vec{k} + \vec{q} \rangle \langle \vec{k} + \vec{q} | w | \vec{k} \rangle}{\frac{\hbar^2}{2m} (k^2 - |\vec{k} + \vec{q}|^2)} \quad (35)$$

The bar above the second term means an averaged value. It should be noted that in performing the sum, we have counted electron-electron interactions twice. Thus it will be necessary to subtract a term equal to the electron-electron interaction; we will do this later on. It should also be mentioned that we must still account for the Coulombic ion-ion interactions.

We will now consider the pseudopotential W to consist of two terms: W_0 , representing the electron-ion interactions; and W_1 , representing the interaction of each electron with the others through a self-consistent potential. Harrison²⁶ has shown that if W is taken to be a local potential, then W is related to W_0 by

$$\langle \vec{k}+\vec{q} | w | \vec{k} \rangle = \frac{\langle \vec{k}+\vec{q} | w_o | \vec{k} \rangle}{\epsilon(q)} \quad (36)$$

$\epsilon(q)$ is the Hartree dielectric function given by

$$\epsilon(q) = 1 + \frac{me^2}{2\pi k_F \hbar^2} \left(\frac{1}{\eta^2} + \frac{1-\eta^2}{2\eta^3} \ln \left| \frac{1+\eta}{1-\eta} \right| \right), \quad (37)$$

where $\eta = q/2k_F$. It then follows that

$$\langle \vec{k}+\vec{q} | w | \vec{k} \rangle = \frac{\langle \vec{k}+\vec{q} | w_o | \vec{k} \rangle}{\epsilon(q)}, \quad (38)$$

where $w_o(r)$ is the bare-ion pseudopotential. The electron-electron interactions thus have the effect of screening the bare ion. The form factor $\langle \vec{k}+\vec{q} | w | \vec{k} \rangle$ is simply related to the unscreened form factor $\langle \vec{k}+\vec{q} | w_o | \vec{k} \rangle$ through the screening function $\epsilon(q)$.

In our work we will only be concerned with local potentials. Then, in Equation 35, $\langle \vec{k} | w | \vec{k}+\vec{q} \rangle$ is independent of $\vec{k}$ and may be taken outside the integral over $\vec{k}$. The resulting integral can then be evaluated and expressed in terms of $\epsilon(q)$;

$$\int_{\vec{k} < k_F} d^3k \frac{1}{\frac{\hbar^2}{2m}(k^2 - |\vec{k}+\vec{q}|^2)} = \frac{\pi^2 q^2}{2e^2} [1 - \epsilon(q)] \quad (39)$$

With the aid of equations 38 and 39, we may rewrite E_{el} as

$$E_{el} = \frac{3}{5}E_F + \overline{\langle \vec{k} | w | \vec{k} \rangle} + \frac{V_o}{8\pi Ze^2} \sum_q S^*(\vec{q}) S(\vec{q}) q^2 \left| \frac{\langle \vec{k}+\vec{q} | w_o | \vec{k} \rangle}{\epsilon(q)} \right|^2 [1 - \epsilon(q)]. \quad (40)$$

We will now correct for the fact that electron-electron interactions have been counted twice. Harrison has shown that the electron-electron energy may be expressed as

$$E_{ee} = \frac{1}{2} \overline{\langle \vec{k} | w_1 | \vec{k} \rangle} + \frac{V_o}{8\pi Ze^2} \sum_q s^*(\vec{q}) s(\vec{q}) q^2 |\langle \vec{k} + \vec{q} | w_1 | \vec{k} \rangle|^2. \quad (41)$$

The first term is the electrostatic energy of a uniform electron charge density in the potential due to this same density; the second term accounts for the nonuniformity of the electron density. If the electrons could be described by plane waves, the charge density would be uniform; the second term would then vanish. Since w_1 is related to w_o by $w_1 = w - w_o$, we have that

$$\langle \vec{k} + \vec{q} | w_1 | \vec{k} \rangle = \frac{\langle \vec{k} + \vec{q} | w_o | \vec{k} \rangle}{\epsilon(q)} [1 - \epsilon(q)], \quad (42)$$

by use of Equation 38. Subtracting Equation 41 from Equation 40, we obtain with the aid of Equation 42 that

$$E'_{el} = E_{el} - E_{ee} = 3/5 E_F + \overline{\langle \vec{k} | w - w_1 / 2 | \vec{k} \rangle} \quad (43)$$

$$- \frac{V_o}{8\pi Ze^2} \sum_q s^*(\vec{q}) s(\vec{q}) q^2 |\langle \vec{k} + \vec{q} | w_o | \vec{k} \rangle|^2 \frac{\epsilon(q) - 1}{\epsilon(q)}.$$

The second term of Equation 43 may be rearranged as

$$\overline{\langle \vec{k} | w - w_1 / 2 | \vec{k} \rangle} = \overline{\langle \vec{k} | w_o + w_1 - w_1 / 2 | \vec{k} \rangle} \quad (44)$$

$$= \overline{\langle \vec{k} | w / 2 | \vec{k} \rangle} + \overline{\langle \vec{k} | v_{Coul} | \vec{k} \rangle} + \overline{\langle \vec{k} | w_o - v_{Coul} | \vec{k} \rangle}.$$

Here v_{Coul} is the ionic Coulomb potential. We still must add to our energy expression the direct Coulomb interaction energy E_{ii} between ions. But $E_{ii} + \langle \vec{k} | \bar{w}_1/2 | \vec{k} \rangle + \langle \vec{k} | v_{\text{Coul}} | \vec{k} \rangle$ is just the electrostatic energy E_c discussed in the jellium model. We then find that

$$E_H = E'_{el} + E_{ii} = \frac{3}{5} E_F + E_c + \langle \vec{k} | \bar{w}_0 - v_{\text{Coul}} | \vec{k} \rangle - \frac{V_o}{8\pi Z e^2} \sum_q S'^* (\vec{q}) S(\vec{q}) q^2 |\langle \vec{k} + \vec{q} | \bar{w}_0 | \vec{k} \rangle|^2 \frac{\epsilon(q) - 1}{\epsilon(q)}. \quad (45)$$

This is the Hartree energy since correlation and exchange have not yet been included. It can be seen that E_H is just the energy of jellium plus first and second order perturbation terms, hereafter referred to as the band structure energy $E_{\text{B.S.}}$.

We will now explicitly add in the correlation and exchange energy of the electron gas. The exchange energy (per electron) is given by

$$E_x = -.916 \frac{e^2}{2r_s}, \quad (46)$$

where r_s is related to the electron density by $\frac{4}{3} \pi r_s^3 = \frac{V_o}{Z}$. The correlation energy is taken to be the Pines-Nozières approximate expression,

$$E_{\text{corr}} = \frac{-e^2}{2a_o} (.115 - .031 \ln(\frac{rs}{a_o})), \quad (47)$$

where $a_o = \frac{\hbar^2}{me^2}$ is the Bohr radius. Our total energy can now be written as

$$\begin{aligned}
 E &= E_H + E_x + E_{\text{corr}} \\
 &= \frac{3}{5} E_F + E_x + E_{\text{corr}} + E_c + E_{\text{B.S.}}, \quad (48)
 \end{aligned}$$

where $E_{\text{B.S.}} = \langle \vec{k} | w_o - v_{\text{Coul}} | \vec{k} \rangle$

$$- \frac{V_o}{8\pi Ze^2} \sum_q s^*(\vec{q}) s(\vec{q}) q^2 |\langle \vec{k} + \vec{q} | w_o | \vec{k} \rangle|^2 \frac{\epsilon(q) - 1}{\epsilon(q)}. \quad (49)$$

We now need to find an appropriate pseudopotential. As discussed earlier, $W(r)$ behaves like $V(r)$ outside the ion core and is small within the core. If we just consider $w_o(r)$, the pseudopotential due to a bare ion, it is a reasonable assumption that $w_o(r)$ is Coulombic outside the core and very small within. It is easiest to simply assume that $w_o(r)$ vanishes completely inside the core region. This is the pseudopotential originally proposed by Ashcroft^{42,43} and used by Suzuki, et al.^{1,2} We thus write that

$$\begin{aligned}
 w_o(r) &= \frac{-Ze^2}{r}, \quad r > r_c \\
 &= 0, \quad r < r_c, \quad (50)
 \end{aligned}$$

where r_c is the "core radius"; this will be the only adjustable parameter occurring in our calculations.

Using this pseudopotential, the form factor is given by⁴³

$$\langle \vec{k} + \vec{q} | w_o(r) | \vec{k} \rangle = - \frac{4\pi Ze^2}{V_o q^2} \cos(qr_c), \quad (51)$$

and it can be shown that

$$\langle \vec{k} + \vec{q} | w_0(r) - v_{\text{Coul}}(r) | \vec{k} \rangle = \alpha \frac{Z}{V_0} \frac{e^2}{2},$$

where

$$\alpha = 4\pi r_c^2.$$

The band structure energy can now be expressed as

$$E_{\text{B.S.}} = \alpha \frac{Z}{V_0} \frac{e^2}{2} - \frac{2\pi Ze^2}{V_0} \sum_q q^{-2} S^*(\vec{q}) S(\vec{q}) \cos^2(qr_c) \frac{\epsilon(q) - 1}{\epsilon(q)}. \quad (52)$$

It is easiest now to work in atomic units. All lengths are measured in units of a_0 , and all energies are in units of Rydbergs per electron. Using the relations $\eta = q/2k_F$ and $k_F^3 = \frac{3\pi^2 Z}{V_0}$, we may rewrite Eq. 52 as

$$E_{\text{B.S.}} = \alpha \frac{Z}{V_0} - \frac{k_F}{3\pi} \sum_{\eta} \eta^{-2} S^*(\vec{q}) S(\vec{q}) \cos^2(2k_F \eta r_c) \frac{\epsilon(\eta, k_F) - 1}{\epsilon(\eta, k_F)}. \quad (53)$$

By combining the kinetic, exchange and correlation energies into one expression E_v , we find that

$$E_v = .6 k_F^2 - \frac{.916}{r_s} - (0.115 - .031 \ln r_s). \quad (54)$$

Our final expression for the energy density is

$$E = E_v + E_c + E_{\text{B.S.}}, \quad (55)$$

where E_v , E_c and $E_{\text{B.S.}}$ are given by Equations 54, 11 and 53 respectively.

E_v depends only upon the atomic volume, and thus this term only contributes to two Fuchs constants, $\frac{\partial^2 E}{\partial v^2}$ and $\frac{\partial^3 E}{\partial v^3}$. 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.

Strain derivatives of the Coulomb energy E_c have already been discussed in the jellium model. A useful relation when differentiating E_c is that $\frac{\partial}{\partial x} \phi_m(x) = -\phi_{m+1}(x)$.

The final expression for the band structure energy is a function of η and k_F . For a v strain, η does not change, since $\eta' = \frac{q'}{2k_F'} = \frac{v^{-1/3} q}{2v^{-1/3} k_F} = \frac{q}{2k_F} = \eta$. For a shear strain, k_F does not change, since it only depends on volume. Thus we need only take derivatives of $E_{B.S.}$ with respect to η and k_F . For example, $\frac{\partial E_{B.S.}}{\partial v} = \frac{\partial E_{B.S.}}{\partial k_F} \frac{\partial k_F}{\partial v}$ and $\frac{\partial E_{B.S.}}{\partial \epsilon} = \frac{\partial E_{B.S.}}{\partial \eta} \frac{\partial \eta}{\partial \epsilon}$. We assume that the core radius r_c does not change during deformation.

For the h.c.p. structure it is easily shown that $S^*(\vec{q})S(\vec{q}) = \cos^2(\frac{1}{2}\vec{q} \cdot \vec{\tau})$, where $\vec{\tau}$ is described in Figure 6. For the case of no internal strain, $\vec{q}' \cdot \vec{\tau}' = \vec{q} \cdot \vec{\tau}$. Strain derivatives of the structure factor thus vanish except for those elastic constants involving the e strain.

We have completed calculations 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 $r_c = 1.38 a_0$ is near the value of $1.39 a_0$ determined by Ashcroft and Langreth⁴³ from a comparison of theory and experiment for the resistivity of liquid magnesium. The value $r_c = 1.358 a_0$ was found by Shyu and Gaspari⁴⁴ from fitting the first zero of the Ashcroft pseudopotential form factor to that of the Heine-Abarenkov "model"²⁶ 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, we have also completed calculations using a modified⁴⁴⁻⁴⁸ dielectric function. The modified function takes into account correlation and exchange effects in the screening of the electrons. If we define $H(q) = \frac{\epsilon(q)}{\epsilon(q)-1}$, then for the Hartree dielectric function $H = 1 + \frac{2\pi k_F^3 a_0}{g(\eta)}$, where $g(\eta) = 1/\eta^2 + \frac{1-\eta^2}{2\eta^3} \ln \left| \frac{1+\eta}{1-\eta} \right|$. Note that H^{-1} directly enters Eq. 53 for our expression for $E_{B.S.}$. For the modified dielectric function, we have that $H = 1 + \frac{2\pi k_F^3 a_0}{g(\eta)} - \frac{q^2}{2(q^2 + \beta k_F^2)}$. Two forms of β were used: the first was introduced by Sham⁴⁵ and used by Shyu and Gaspari,^{44,46,47} where $\beta = 1 + \frac{2}{\pi k_F a_0}$; the second form was used by Wallace,⁴⁸ where $\beta = \frac{2\pi k_F^3 a_0}{.158 + \pi k_F a_0}$. We have found the elastic constant calculations to be extremely insensitive to whichever form of β is used.

Using the experimental³⁶ atomic volume of magnesium, we have found the equilibrium c/a ratios for the five core radii; our results using both the Hartree and the modified dielectric functions are presented in Table 12. Each c/a was found by numerically solving $\frac{\partial E}{\partial \epsilon} = 0$. 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 we immediately see that our procedure is not successful when applied to a h.c.p. metal such as zinc, for which $c/a = 1.856$. However, the inclusion of a closed-core repulsion term in the energy expression may then yield satisfactory results for zinc. (Core interactions for magnesium can be neglected, as borne out by the elastic constant calculations.)

Knowing c/a for each r_c , we then calculated the internal strain parameter A discussed earlier. A is determined from the condition $A = - \left(\frac{\partial^2 E}{\partial w \partial e} / \frac{\partial^2 E}{\partial w^2} \right)_{e=0}$. Again only the Coulomb and band structure energies contribute

Table 12. Equilibrium values of c/a for various values of r_c . The experimental value of c/a for magnesium is 1.6228.³⁶

r_c (units of a_0)	c/a	
	Hartree	Modified
1.22	1.6413	1.6414
1.34	1.6337	1.6316
1.358	1.6327	1.6304
1.38	1.6315	1.6291
1.50	1.6259	1.6236

here. The results are given in Table 13. We can see that the band structure contributes importantly to the internal strain. For the jellium model, in which the band structure energy is neglected, we found that $A = .8575$ a. Inclusion of the band structure considerably reduces the internal strain, as can be seen in Table 13.

Table 13. Internal strain parameter for various values of r_c .

r_c (units of a_0)	A (units of lattice parameter a)	
	Hartree	Modified
1.22	.326	.223
1.34	.374	.335
1.358	.383	.350
1.38	.394	.368
1.50	.461	.460

We have yet to take into account another equilibrium condition, namely that $\frac{\partial E}{\partial v} = 0$. We have calculated $\frac{\partial E}{\partial v}$ for magnesium using the observed atomic volume, and we found that equilibrium was not satisfied. We then determined the atomic volume for which $\partial E/\partial v = 0$, and found this value to be 30% lower than that of experiment; we did the calculations with $r_c = 1.358 a_0$, the core radius which gives the best agreement of the calculated elastic constants with experiment, as will be seen later. In order to have our energy expression satisfy equilibrium at the observed atomic volume, it is thus necessary to adjust one of our parameters. Suzuki, et al.,^{1,2} as well as Ashcroft and Langreth,⁴³ have chosen to adjust the parameter α of Equation 53. We will adopt that procedure here. α will then be determined by requiring that $\partial E/\partial v = 0$ at the observed atomic volume; we will be able to compare this value with the value $4\pi r_c^2$ calculated from the pseudopotential. Suzuki² has referred to this comparison as a consistency check of the binding energy expression.

It is unfortunate that α need be adjusted; there is no justification in doing so, but an adjustment must be made somewhere in order to have equilibrium at the observed atomic volume. We are in agreement with Suzuki, et al. that the reason for the binding energy not being minimum at the observed atomic volume is mainly due to the volume-dependent energy term E_v ; this term contains an approximate expression for the correlation and exchange energy. It will be seen that with $r_c = 1.358 a_0$, four of the five second order Fuchs elastic constants are in good agreement with experiment. The other constant, $\partial^2 E/\partial v^2$, 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;

the results of these adjustments all resulted in a poorer value for $\partial^2 E / \partial v^2$. Since an adjustment is necessary, the α adjustment seems best in that it results in a better value for $\partial^2 E / \partial v^2$. We feel that the pseudopotential method is successful in predicting 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 $\partial^2 E / \partial v^2$ and $\partial^3 E / \partial v^3$, do depend on E_v and thus cannot be determined as well because of the approximations contained in E_v .

We have already found c/a and the internal strain parameter A for five core radii; by requiring that $\partial E / \partial v = 0$ at the observed atomic volume, we then calculated the second and third order elastic constants. Our results are given in Table 14. We have compared the second order Fuchs constants and the third order Brugger constants with experiment. Since four second order Brugger constants (all but c_{44}) depend on $\partial^2 E / \partial v^2$, we did not make a comparison for them; we felt the comparison would be distorted by the effect of $\partial^2 E / \partial v^2$. For the same reason, we did not compare the pressure derivatives of the elastic constants, since they are dependent upon $(\partial^2 E / \partial v^2)^{-1}$. (A fair comparison might be made by using the experimental value of $\partial^2 E / \partial v^2$ in the determination of the second order Brugger constants and their pressure derivatives; we will make such a comparison later.)

The purpose of Table 14 is to determine the core radius r_c for which the calculated elastic constants best agree with experiment. We have listed the results obtained by using both the Hartree and the modified dielectric function; it can be seen that the results are rather insensitive to whichever dielectric function is used. We feel that using $r_c = 1.358 a_0$ (with the modified dielectric function) gives the best overall agreement with experiment,

Table 14. Elastic constant calculations using a pseudopotential method. Entries are in units of 10^{12} dynes cm^{-2} .

	Calculated Values										Exp. values ³⁶
$r_c =$	1.22 a_o		1.34 a_o		1.358 a_o		1.38 a_o		1.50 a_o		
	Har.	Mod.	Har.	Mod.	Har.	Mod.	Har.	Mod.	Har.	Mod.	
$\partial^2 E / \partial \epsilon^2$	0.502	0.420	0.768	0.742	0.817	0.801	0.880	0.875	1.277	1.340	0.728
$\partial^2 E / \partial e^2$	0.121	0.116	0.189	0.196	0.200	0.209	0.215	0.226	0.297	0.317	0.202
$\partial^2 E / \partial v^2$	0.262	0.237	0.295	0.275	0.303	0.284	0.313	0.296	0.392	0.386	0.382
$\partial^3 E / \partial \gamma^2$	0.091	0.088	0.162	0.171	0.174	0.186	0.191	0.205	0.292	0.320	0.198
$\partial^2 E / \partial \epsilon \partial v$	-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

although the preference over choosing $r_c = 1.38 a_0$ (with the Hartree dielectric function) was very slight. For $r_c = 1.358 a_0$, we have determined α from the condition that $\partial E / \partial v = 0$ at the observed atomic volume. We found that $\alpha = 27.91 a_0^2$; the theoretical value is $4\pi r_c^2 = 23.17 a_0^2$. The agreement of α with $4\pi r_c^2$ is fair; a better expression for E_v may improve the agreement. We have also calculated the binding energy E (Eq. 55) using $r_c = 1.358 a_0$ and the modified dielectric function. Our result is $E = -0.886$ Rydbergs/electron, which is in reasonable agreement with the experimental value of -0.890^{43} Rydbergs/electron.

The values in Table 14 include the contributions from internal strain. So that we may see the effect of the internal strain on the elastic constants, we have listed in Table 15 the calculated values found both by including and neglecting internal strain. The values shown are those obtained by using $r_c = 1.358 a_0$ 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. (We will soon see, however, that internal strain contributions to the Fuchs constants are not small.) It can also be seen that the inclusion of internal strain does improve the overall agreement with experiment.

So that we may see the relative contribution of the electrostatic and band structure energy terms to the elastic constants, we have listed the separate contributions in Table 16. We have not listed the constants which have a contribution from the volume-dependent energy term. It can be seen that $\partial^2 E / \partial v^2 = c_{44}$ is determined primarily from the electrostatic energy, as mentioned at the beginning of this section. For most of the other constants,

Table 15. Internal strain contributions to the third order elastic constants of Mg. Entries are in units of 10^{12} dynes cm^{-2} .

	<u>Calculated values</u>		<u>Exp. values</u> ³⁶
	<u>Without internal strain</u>	<u>With internal strain</u>	
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

Table 16. 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} dynes cm^{-2} .

	<u>Electrostatic Contribution</u>	<u>Band Structure Contribution</u>	<u>Internal Strain Contribution</u>	<u>Calculated Value</u>	<u>Experimental Value</u> ³⁶
$\partial^2 E / \partial \epsilon^2$	1.306	-0.505	-	0.801	0.728
$\partial^2 E / \partial e^2$	0.303	-0.059	-.035	0.209	0.202
$\partial^2 E / \partial \gamma^2$	0.170	0.016	-	0.186	0.198
$\partial^2 E / \partial \epsilon \partial v$	0.001	-0.010	-	-0.009	-0.002
$\partial^3 E / \partial \epsilon^3$	3.10	-3.39	-	-0.29	-2.90
$\partial^3 E / \partial e^3$	0.36	-0.43	0.32	0.25	0.40
$\partial^3 E / \partial \epsilon \partial v^2$	-0.00	0.03	-	0.03	0.01
$\partial^3 E / \partial v \partial \epsilon^2$	-0.44	-1.51	-	-1.95	-1.73
$\partial^3 E / \partial v \partial \gamma^2$	-0.06	-0.38	-	-0.44	-0.29
$\partial^3 E / \partial \epsilon \partial \gamma^2$	-0.84	0.15	-	-0.69	-0.81
$\partial^3 E / \partial e \partial \gamma^2$	-0.11	0.45	-0.40	-0.06	-0.06
$\partial^3 E / \partial v \partial e^2$	-0.10	-0.49	0.17	-0.42	-0.32
$\partial^3 E / \partial \epsilon \partial e^2$	0.32	0.77	0.33	1.42	1.60

however, the band structure contribution is large. This was not so in the case of the alkali¹ ($Z=1$) metals; for aluminum² ($Z=3$), however, the band structure effects were also found to be large. Harrison²⁶ has also noticed the increase in band structure contributions for higher valence; he has stated 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 $Z = 1$ (alkali¹ metals), good for $Z = 2$ (Mg, present work), and fair for $Z = 3$ (Al²).

It can be seen from Tables 15 and 16 that the calculated Fuchs constants are not in as good agreement with experiment as are the Brugger constants. There are several reasons for this. First of all, the experimental Fuchs constants have been determined from the appropriate linear combinations of the experimental Brugger constants; due to propagation of errors, the Fuchs experimental constants are not known as accurately as the Brugger constants. Also, internal strain contributions are more significant in the case of the Fuchs constants; the internal strain makes a major contribution to the Fuchs constants, but only a small contribution to the Brugger constants. There are also some large cancellations between the electrostatic and band structure contributions to the Fuchs constants, and we suspect that this may not occur for the Brugger constants. Such cancellations have occurred for $\partial^3 E / \partial \epsilon^3$, which is the only constant in poor agreement with experiment. It can be seen from Table 16 that both the electrostatic and band structure contributions to $\partial^3 E / \partial \epsilon^3$ are very large; however, the contributions are of opposite sign, and considerable cancellation thus occurs. In addition, there is a significant

amount of uncertainty in the experimental value of $\partial^3 E / \partial \epsilon^3$; this can be seen by expressing $\partial^3 E / \partial \epsilon^3$ in terms of the Brugger constants. From Table 10,

$$\frac{\partial^3 E}{\partial \epsilon^3} = 9 \frac{\partial^2 E}{\partial \epsilon \partial v} + \frac{1}{4} \begin{pmatrix} -2c_{111} + c_{222} - 3c_{112} + 6c_{113} \\ -12c_{133} + 4c_{333} + 6c_{123} \end{pmatrix}.$$

Using the experimental values of $\frac{\partial^2 E}{\partial \epsilon \partial v}$ and of the third order Brugger constants, we find that

$$\begin{aligned} \frac{\partial^3 E}{\partial \epsilon^3} &= 9(-.002) + \frac{1}{4} \begin{pmatrix} 13.26 - 8.64 + 5.34 + 1.80 \\ +10.32 - 29.04 - 4.56 \end{pmatrix} \\ &= -2.90 \times 10^{12} \text{ dynes cm}^{-2}. \end{aligned}$$

We thus see that considerable cancellation has also taken place in the determination of the experimental value of $\partial^3 E / \partial \epsilon^3$. We feel that the errors in the experimental values of the third order Fuchs constants are considerably larger than the errors for the third order Brugger constants.

We mentioned earlier that we did not compare the calculated second order Brugger constants and their pressure derivatives with experiment because of the effect of $\partial^2 E / \partial v^2$; we will now make this comparison. We have used the experimental value of $\partial^2 E / \partial v^2$, together with the calculated values of the four other second order Fuchs constants, to determine the five second order Brugger constants. We then determined the pressure derivatives of the second order constants; for this we used the calculated values of the third order Brugger constants (Table 15). Our results are given in Table 17. The agreement with experiment is very good for the second order constants and for

$\frac{dc_{66}}{dP}$, but only fair ($\sim 20\%$) for the other pressure derivatives; we have found, however, that better ($\sim 10\%$) agreement of these pressure derivatives with experiment could be obtained by 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.

Table 17. 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} dynes cm^{-2} , and the pressure derivatives are dimensionless.

	<u>Calculated value</u>	<u>Exp. value</u> ³⁶
c_{11}	.686	.666
c_{12}	.268	.262
c_{13}	.201	.219
c_{44}	.186	.198
c_{33}	.726	.702
$c_{66} = \frac{1}{2}(c_{11} - c_{12})$	.209	.202
$\frac{dc_{44}}{dP}$	1.40	1.60
$\frac{dc_{66}}{dP}$	1.36	1.37
$\frac{dc_{11}}{dP}$	5.19	6.23
$\frac{dc_{33}}{dP}$	5.89	7.29

IV. SUMMARY AND CONCLUSIONS

The complete set of the ten third order elastic constants of magnesium has been determined experimentally from measurements of the hydrostatic pressure and uniaxial compression derivatives of the natural sound velocities using a variation of the pulse superposition technique. The specimen was neutron irradiated to suppress dislocation effects.

A theoretical model was 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 cubic metals. The only adjustable parameter was the core radius r_c .

Because magnesium exists in the hexagonal close-packed structure, certain features entered that were absent in the case of the cubic metals. It was necessary to require that the energy density be a minimum with respect to the c/a ratio; the equilibrium c/a ratio was calculated and found to be very close to the experimental value. The cubic metals considered by Suzuki, et al. were primitive, meaning there was only one atom per unit cell. The h.c.p. structure, however, consists of two interpenetrating hexagonal lattices, and there are two atoms per unit cell. Since the h.c.p. structure is non-primitive, 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 found that the energy density did not satisfy the equilibrium condition $\frac{\partial E}{\partial v} = 0$ 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. It is felt that the volume-dependent energy term is least accurate because of the approximate expression for the correlation and exchange energy. It was seen that the volume-dependent energy term did not contribute to four of the second order Fuchs elastic constants, and that the calculated values of these constants were in good agreement with experiment. The other constant, $\frac{\partial^2 E}{\partial v^2}$, did contain a volume-dependent contribution, and the calculated value of $\frac{\partial^2 E}{\partial v^2}$ was only in fair agreement with experiment.

Fuchs-type strain parameters were employed in calculating the elastic constants; the calculations were done for five different core radii in order to determine the r_c which gives the best agreement between theory and experiment. Both the Hartree and the modified dielectric function were used; the results were found to be rather insensitive to whichever dielectric function is used. The calculated elastic constants were seen to be in best agreement with experiment 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 value $1.358 a_0$ had been determined previously by Shyu and Gaspari from fitting the Ashcroft form factor to that of the Heine-Abarenkov "model" pseudopotential; the value $1.38 a_0$ is near the value ($1.39 a_0$) determined from a comparison of theory and experiment for the resistivity of liquid magnesium.

It was found that internal strain contributions to the Brugger elastic constants were small, but that the contributions to the Fuchs constants were significant. The inclusion of internal strain contributions was seen to improve the overall 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 ($Z = 3$). It was concluded that band structure contributions increase with higher valence; thus it is more difficult to obtain quantitative results for higher Z , since the errors in the band structure energy have a greater effect on the calculated values. The elastic constant calculations were seen to bear this out; the agreement with experiment was excellent for $Z = 1$, good for $Z = 2$, and fair for $Z = 3$.

There are two major points of significance that can be drawn from this work. The first point is the success of pseudopotential theory in predicting both the mechanical and electronic properties of magnesium. The core radius determined from elastic constant calculations was found to be 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 gives one confidence in its use in other calculations. The agreement with experiment of the calculated elastic constants was found to be good; this comparison, however, was really a very 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.⁴⁹

The second major point is that the results of this work represent the most accurate agreement between theory and experiment for the third order elastic constants of a metal. 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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29. We have found two discrepancies with Cousin's results. Our results for g_8 differ from his in sign, and our results for g_5 differ in magnitude. However, Cousins's value for g_5 depends on g_8 ; if the sign of his g_8 were changed and g_5 then recalculated, his results would agree exactly with ours. Internal consistency was provided in our calculation in that the Cauchy relations held for the electrostatic contributions to the Brugger constants; these relations must hold since the electrostatic potential is central.
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36. Our calculations are valid at 0°K in the absence of zero-point vibrations. At room temperature the lattice parameters of magnesium are³⁸ $a = 3.2094 \text{ \AA}$ and $c = 5.2105 \text{ \AA}$. Using the thermal expansion data of Goens³⁹ and Schmid, we have found the lattice parameters at 0°K. The extrapolation was linear to exclude zero-point effects. Our results are $a = 3.1838 \text{ \AA}$ and $c = 5.1665 \text{ \AA}$, for which $c/a = 1.6228$ and $V_0 = \sqrt{3} a^2 c / 4 = 22.677 \text{ \AA}^3$. For experimental values of the second order constants, we have used the linearly-extrapolated 0°K values of Leibfried⁴⁰ and Ludwig. The experimental values of the pressure derivatives and the third order constants are the room temperature values reported in the experimental section of this paper.

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