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# Calculation of the Elastic Shear Constants of Magnesium and Magnesium Alloys*

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Leigh's calculation of the elastic shear constants of aluminum are extended to include crystals of lower symmetry, and the results are used to interpret the constants of pure magnesium and dilute magnesium alloys. The requirement that pure magnesium be in equilibrium with respect to shears that change the $c/a$ ratio of this hexagonal crystal is consistent only with the assumption that electron overlap has already occurred across the Brillouin zone faces perpendicular to the $c$ axis, a result which is at variance with the usual assumptions for this metal. Assuming $c$ overlap and one other type of electron overlap in the pure metal, it is found that the total number of overlap electrons (or, equivalently, the number of holes) is $1.70\times 10^{21}$ per cm$^3$, i.e. 2% of the valence electron density. The overlap which appears at an electron/atom ratio of 2.01 is assumed to be an overlap in the equatorial plane of Brillouin zone; this overlap produces an abrupt change in one of the shear constants as the electron/atom ratio is increased beyond 2.01, a behavior of the type predicted by Leigh for aluminum-zinc alloys. The abrupt change in the constant is characteristic of $T=0$°K, however; at room temperature, the predicted effect is much more gradual and is found to agree with the experimental results.

## 1. INTRODUCTION

FOR the monovalent metals it is generally assumed that there are two important contributions to the elastic shear-strain energy of the crystal: (1) a purely electrostatic term representing the difference of electrostatic energy of the ion cores in the strained and unstrained geometry, and (2) a term arising from change in the short-range repulsive interaction of the ion cores. For metals of higher valency, an additional term derives from the change in Fermi energy, caused by movements of the Brillouin zone planes as the metal is sheared. Leigh[1] has proposed a method for calculating these changes in Fermi energy in a cubic metal, and has used his results to obtain the shear constants of trivalent aluminum.

Another metal of great theoretical interest is magnesium. Magnesium has the close-packed hexagonal structure, is divalent, and therefore has just enough electrons to fill the second Brillouin zone. But magnesium is a metal; hence, it has holes in the second zone and an equal number of electron overlaps into higher zones. Electronic specific-heat and magnetic-susceptibility data give the combined density of states (at the Fermi surface) of these overlaps and holes, but not the total number of either. The elastic constants of magnesium have been measured by several authors,[2–4] and, recently, the elastic constants of magnesium alloys of electron-atom ratio in the range 1.996–2.020 have been measured by Long and Smith.[4] One purpose of the present paper is to extend Leigh's theory of the elastic shear constants to include metals of lower symmetry, in particular to those with the close-packed hexagonal structure. Although the lower symmetry of magnesium complicates the calculation of Fermi energy slightly, it provides an additional relationship from which one can infer something about the number of overlap electrons and holes. The requirement that the metal be in equilibrium with respect to shears which change the $c/a$ ratio of the metal allows one to determine uniquely the number of overlaps and holes provided only one type of overlap and one type of hole are present in the band structure of the metal. Magnesium apparently has two types of overlap and one type of hole, so that the equilibrium requirement does not determine these uniquely, but merely provides a relationship between them.

In addition to his work on pure aluminum, Leigh predicted a rather interesting behavior in one of the shear constants, $\frac{1}{2}(c_{11}-c_{12})$, of aluminum+divalent metal as a function of composition of the alloy. This behavior consists of an abrupt decrease in the constant as the electron/atom ratio is increased beyond the point where a new electron overlap is initiated across one or more of the Brillouin zone faces. Unfortunately, this part of Leigh's theory has not been subjected to experimental verification because of the severe experimental difficulties involved in obtained single crystals of the proper composition and structure. In magnesium, however, both lattice parameter measurements[5] and transport phenomena investigations[6] of the dilute alloys have indicated the initiation of new zone overlaps at about 2.01 electrons per atom; hence, it appeared that Leigh's theory could be tested with this alloy system. The essentially negative results found by Long and Smith[4] led the present authors to reexamine Leigh's theory. The measurements were made at room temperature, and Leigh's theory is strictly applicable at absolute zero. Extension of Leigh's results to room

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* Work supported in part by the Office of Naval Research, in part by the National Carbon Company (A Division of Union Carbide and Carbon Corporation).

[1] R. S. Leigh, Phil Mag. 42, 139 (1951).

[2] E. Goens and E. Schmid, Physik. Z. 37, 385 (1936).

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 67, 29 (1932).

[4] T. R. Long and Charles S. Smith, Acta Metallurgica (to be published).

[5] W. Hume-Rothery and G. V. Raynor, *The Structure of Metals and Alloys* (The Institute of Metals, London, 1954), pp. 166–167.

[6] A. I. Schindler and E. I. Salkovitz, Phys. Rev. 91, 1320 (1953).

temperature shows that the predicted change in shear constant is much more gradual as one goes through the critical electron-atom ratio; and, indeed, the predicted curve agrees with the experimental values. This topic will be discussed in more detail in Sec. 6.

## 2. ELASTIC STRAIN ENERGY OF MAGNESIUM

Magnesium is a close-packed hexagonal metal with nearly ideal $c/a$ ratio ($c/a=1.6237$). There are five independent elastic constants, and the strain energy of the crystal is usually written

$$W=W_0+\tfrac{1}{2}c_{11}(e_x^2+e_y^2)+\tfrac{1}{2}c_{33}e_z^2+c_{12}e_xe_y +c_{13}(e_xe_z+e_ye_z)+\tfrac{1}{2}c_{44}(\gamma_1^2+\gamma_2^2)+\tfrac{1}{4}(c_{11}-c_{12})\gamma_3^2, \quad (1)$$

where $e_x$. $e_y$, $e_z$ are normal strains, and the $\gamma$'s are changes in angles between the principal axes of the crystal. Three of the elastic constants may be taken as pure shears, and it is convenient to define the following set:

$$C\equiv c_{11}+c_{12}+2c_{33}-4c_{13}, \quad C'\equiv\tfrac{1}{2}(c_{11}-c_{12}), \quad c_{44}.$$

$C$ corresponds to a strain which changes the $c/a$ ratio at constant volume, leaving the symmetry of the crystal unchanged; $C'$ corresponds to a shear which changes the angle between any pair of orthogonal axes in the basal plane of the crystal, leaving the $c$ axis unaffected; and $c_{44}$ corresponds to a shear which tilts the $c$ axis with respect to the basal plane.

For convenience in calculating contributions to the strain energy of the solid under the appropriate shear, it is expedient to write the lattice vectors in terms of a strain parameter: $\xi$, $\eta$, or $\epsilon$. For $C$, the direct and reciprocal lattice vectors may be written

$$\begin{aligned}
a_1&=a\xi^{\frac{1}{3}}(1,0,0),\\
a_2&=a\xi^{\frac{1}{3}}(-\tfrac{1}{2}, \sqrt{3}/2, 0),\\
a_3&=c\xi^{\frac{1}{3}}(0,0,\xi^{-1});\\
b_1&=(2\pi/\xi^{\frac{1}{3}}a)(1,1/\sqrt{3},0),\\
b_2&=(2\pi/\xi^{\frac{1}{3}}a)(0,2/\sqrt{3},0), \qquad (2)\\
b_3&=(2\pi/\xi^{\frac{1}{3}}c)(0,0,\xi);
\end{aligned}$$

and the shear constant $C$ is then given by

$$C=(9/2)(d^2W/d\xi^2)_0, \qquad (3)$$

where the subscript 0 indicates that the derivative is computed at zero strain, viz., $\xi=1$.

For $C'$ and $c_{44}$, only the direct lattice vectors will be given:

$$\begin{aligned}
a_1&=a\eta^{\frac{1}{2}}(1,0,0),\\
a_2&=a\eta^{\frac{1}{2}}(-\tfrac{1}{2}, \sqrt{3}/2\eta, 0),\\
a_3&=c(0,0,1),
\end{aligned}$$

with

$$C'=(d^2W/d\eta^2)_0; \qquad (4)$$

$$\begin{aligned}
a_1&=a(1,0,\epsilon),\\
a_2&=a(-\tfrac{1}{2}, \sqrt{3}/2, -\tfrac{1}{2}\epsilon)\\
a_3&=c(0,0,1),
\end{aligned}$$

with

$$c_{44}=(d^2W/d\epsilon^2)_0. \qquad (5)$$

Zero strain corresponds to $\eta=1$ and $\epsilon=0$.

Since the crystal is under no external stress at zero strain, we have as the condition for equilibrium

$$(dW/dx)_0=0, \qquad (6)$$

where $x$ stands for one of the strain parameters, $\xi$, $\eta$, or $\epsilon$.

As mentioned in Sec. I, it is customary to think of each shear constant as composed of three parts: (1) an electrostatic term, (2) a term due to the interpenetration of the ion cores, and (3) the Fermi term. The ion cores in magnesium are rather small, and direct calculation by Huntington[7] has indicated that the core-interpretation term contributes at most a few percent to each shear constant. We shall, therefore, make very little error if we neglect this contribution completely. Now, Raimes[8] has shown that the $\mathbf{k}=0$ wave function in magnesium is very flat near the boundary of the Wigner-Seitz cellular polyhedron; hence, this level does not make an appreciable contribution to the Fermi term. In other words, the Fermi term arises from electrons of $\mathbf{k}\neq 0$, whose energy changes in first approximation are the energy changes experienced by free electrons at equivalent points in the Brillouin zone.

Following Leigh[1] we break up the Fermi term (subscript $F$) into two parts, a full-zone contribution (superscript I), and an overlap-hole contribution (superscript II), which are subsequently treated independently. The full-zone calculation treats the Brillouin zone as fully occupied, allowing for energy changes through the movement of Brillouin zone planes; the overlap-hole contribution, on the other hand, provides for displacement of the Fermi surface during the distortion and the simultaneous transfer of electrons from certain overlap positions to others.

The decomposition of an elastic constant into several parts is not unique unless the corresponding parts of the first derivative, $(dW/dx)_0$, are each zero separately. In other words, if the total strain energy is written as $W_1+W_2$, and if $(dW_1/dx)_0$ and $(dW_2/dx)_0$ are not each zero, then $(d^2W_1/dx^2)_0$ does not necessarily equal $(d^2W_1/dy^2)_0$, where $y$ is a strain parameter corresponding to the inverse shear to that which $x$ corresponds. Hence, the decomposition is characteristic of *one* of the group of strains which give the desired elastic constant. Despite this shortcoming, the decomposition is still a useful concept and leads to no difficulty as long as Eq. (6) is obeyed by the *total* strain energy.

## 3. COULOMB TERM

The electrostatic or Coulomb contributions to the three elastic shear constants of magnesium have been computed by Huntington[9] by means of the Ewald

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[7] H. B. Huntington, Phys. Rev. **57**, 60 (1940).

[8] S. Raimes, Phil. Mag. **41**, 568 (1950).

[9] H. B. Huntington (private communication). The results quoted in reference 7 are in error by a factor of two.

method on the assumption that the doubly-charged ion cores move in an electron sea of uniform density. These results, which are given in Table I, represent in fact the maximum Coulomb contributions. Leigh[1] has shown that a nonuniform electron density can reduce this term by as much as 25%, and relaxation effects, which have been predicted by several authors,[10,11] should reduce it even farther. We believe that the combined effect of nonuniform electron density and relaxation will be such as to reduce each value in Table I to about one-half the value given there.

The first derivatives of the Coulomb energy,

$$(dW_{\text{Coul}}/d\eta)_0 \quad \text{and} \quad (dW_{\text{Coul}}/d\epsilon)_0,$$

are identically zero. $(dW_{\text{Coul}}/d\xi)_0$ is zero at the ideal $c/a$ ratio; at other values of $c/a$ the derivative may be approximated by $(2/9)C_{\text{Coul}}\Delta\xi$, where $C_{\text{Coul}}$ is the Coulomb contribution to $C$.

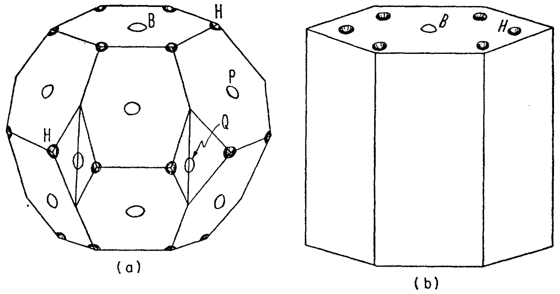
TABLE I. Maximum electrostatic contribution to the three elastic shear constants of magnesium.

| Constant | Max. electrostatic term (dynes/cm$^2$) |
|---|---|
| $C$ | $2.55\times10^{12}$ |
| $\frac{1}{2}(c_{11}-c_{12})$ | $0.297\times10^{12}$ |
| $c_{44}$ | $0.162\times10^{12}$ |

## 4. FERMI TERM

Magnesium, being divalent and having two atoms per unit cell, requires a consideration of the first and second Brillouin zones of the hexagonal lattice; for simplicity this combination will be referred to as the Brillouin zone (B.Z.) of magnesium. The B.Z. is shown in Fig. 1(a), while the double-sized hexagonal prism, Fig. 1(b), which is obtained by translating various segments of 1(a) through vectors of the reciprocal lattice, is included for ease of visualization. If the one-electron energies were accurately known as a function of **k**, either of the zones 1(a) or 1(b) would be a proper one to use. We wish to use the nearly-free electron approximation, however; hence, it is necessary that the B.Z. be as nearly spherical as possible. This limits us to the first choice, Fig. 1(a). It is an interesting fact that the "free-electron energy" of zone 1(a) at the ideal $c/a$ ratio is only one percent greater than that of a sphere of equal volume.

The positions of the holes in the B.Z. are rather easy to pick out; they are marked by the symbol $H$ in Fig. 1(a). The hole at the most distant part of the equatorial section of the zone and the hole at the corner of the top face of the zone are, in fact, part of the same hole, as is seen more clearly in Fig. 1(b) where these two segments of the B.Z. have been brought into coincidence. The holes make up six complete spheroids.



(a) (b)

FIG. 1. (a) The Brillouin zone of magnesium, showing the positions of electron overlap and holes. (b) The double-sized prism zone obtained by translating some of the segments in (a) through a vector of the reciprocal lattice.

The electron overlap positions are more speculative since there are a number of possibilities; on the nearly-free electron model we would pick out three different cases: (1) $B$ overlap, across the faces perpendicular to the $c$ axis, (2) $P$ overlap across the slant faces, and (3) $Q$ overlap (in the equatorial plane). As is seen from the figure, $B$ overlap consists of just one pair, or one complete spheroid, $P$ overlap six spheroids, and $Q$ overlaps two spheroids. It is generally assumed that both $P$ and $Q$ overlaps occur in pure magnesium, whereas the $B$ overlap first occurs in magnesium alloys at an electron-atom ratio greater than 2.01, the reason for this assumption being that abrupt changes are observed[5] in $c$ lattice parameter *versus* composition but not in the $a$ parameter. The results of the present paper, however, do not support this assumption. As will be seen in Sec. 6, it must be assumed the $B$ overlap has already occurred in pure magnesium in order that the metal be in equilibrium with respect to the shear which changes the $c/a$ ratio.

### Full Zone Contribution

By dividing the B.Z. into tetrahedra as proposed by Leigh,[1] the full zone contributions to each of the shear constants may be calculated. One such tetrahedron is shown in Fig. 2, the lengths $p$, $q$, and $r$ being mutually orthogonal. As suggested by Leigh, the one-electron energy is approximated by

$$E(\mathbf{k})=\alpha_0(\hbar^2/2m)[k^2-\lambda\{p^2(k_z/p)^{2/\lambda} + q^2(k_y/q)^{2/\lambda}+r^2(k_x/\lambda)^{2/\lambda}\}], \quad (7)$$

where $k_z$, $k_y$, $k_x$ are measured along $p$, $q$, and $r$, respectively, $\lambda$ is a parameter between 0 and 1.0, and $\alpha_0$ is the inverse effective-mass ratio $(m/m^*)$ for the bottom of the band. The contribution to the Fermi energy by each tetrahedron is then

$$(W_{\text{F}}^{\text{I}})_{\text{tet}}=(\alpha_0/4\pi^3)(\hbar^2/2m)(pqr/10) \times[Fp^2+Gq^2+Hr^2], \quad (8)$$

where

$$F=1-5\lambda^2/(2+3\lambda),$$
$$G=0.5-5\lambda^3/(2+3\lambda)(1+\lambda),$$
$$H=(1/6)-5\lambda^4/(2+3\lambda)(1+\lambda)(2+\lambda).$$

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[10] C. Zener, Acta Cryst. 3, 346 (1950).
[11] H. B. Huntington, Phys. Rev. 91, 1092 (1953).

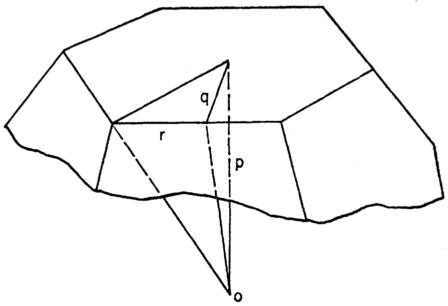

FIG. 2. View of part of the Brillouin zone, showing one of the tetrahedra used to compute the full-zone energy.

Since $p$, $q$, and $r$ are functions of the strain parameter, the contribution to the elastic constant may be obtained by differentiation. It was found that both the first and second derivatives of the full zone energy are fairly insensitive to the value of $\lambda$, particularly if $\alpha_0$ and $\lambda$ are varied simultaneously in such a way that the width of the band is unchanged. The actual values used in the following section are those for $\lambda=0$.

For calculating $C$, seven different tetrahedra (one taken negatively) were required, whereas for $C'$ eighteen different ones were needed. The full zone contribution to $c_{44}$, which distorts the crystal into an even lower symmetry, was not computed. $(dW_F{}^{\mathrm{I}}/d\xi)_0$ is not zero; at the ideal $c/a$ ratio it is $-18\alpha_0\times 10^9$ ergs cm$^{-3}$ for magnesium. The other two first derivatives are identically zero at all $c/a$ ratios.

By dividing the Fermi term into two parts, the contribution of each hole is handled in two distinct ways: in the full zone term the energy of the *full* hole is computed along with the energy of the rest of the zone; in the overlap-hole term the energy of the *full* hole is subtracted away. It is important that these two methods be consistent with each other in order that no spurious contribution to the elastic constants creep into the calculation. We should like to point out that Leigh's expression (7) is consistent with inverted spherical energy surfaces for the holes, as long as the holes are not too large and $\lambda$ not too small. This is easily demonstrated: the hole will appear in the corner of the tetrahedron where $\mathbf{k}$ is a maximum; hence, we may develop $\mathbf{k}$ about this maximum value ($k_z=p-\kappa_z$, etc.). Substituting in (7), we find that the linear term in $\boldsymbol{\kappa}$ vanishes, and from the quadratic term the effective mass of the hole is found to be $m\lambda/[2\alpha_0(1-\lambda)]$. But the results of the full-zone contribution are not very dependent on $\lambda$; thus, any effective mass is consistent with the full-zone calculation.

## Overlap-Hole Contribution

It will be assumed that the energy surfaces of each overlap region, or hole, move rigidly with the B.Z. face as the metal is sheared. Since each overlap, or hole, is "filled" to the Fermi level $\zeta$ which is characteristic of the Fermi surface as a whole, electrons will transfer from certain overlap (or hole) positions to others as the metal is sheared. We use the same notation as Leigh, the subscript $i$ denoting the type of overlap (or hole), $j$ the number of pairs of each type, and $E_{ij}$ the energy of the origin of each overlap (or hole). $N_i(E-E_{ij})$ is the density of states per unit energy range in each pair of type $i$, and $n_{ij}$ the total number of carriers in each pair. $n_{ij}$ is positive if it refers to an overlap, and *negative* if it refers to a hole.

The total number of overlaps minus the total number of holes is a constant, independent of the state of shear of the crystal; mathematically,

$$n=\sum_{ij}n_{ij}=\text{constant}, \tag{9}$$

where for pure magnesium the constant is *zero*, for alloys with the same structure the constant depends uniquely on the electron-atom ratio. Hence, both

$$(dn/dx)_0=0, \quad \text{and} \quad (d^2n/dx^2)_0=0, \tag{10}$$

where $x$ is one of the strain parameters: $\xi$, $\eta$, or $\epsilon$.

Now each $n_{ij}$ is related to $N_i(E-E_{ij})$ by the expression

$$n_{ij}=\pm\int_0^{|\zeta-E_{ij}|}N_i(\omega)d\omega, \tag{11}$$

where the + sign refers to overlaps, the − to holes. Combining (9) and (11) with the first expression in (10), we obtain for the shift in Fermi level:

$$(d\zeta/dx)_0=[\sum_{ij}N_i(|\zeta-E_{ij}|)]^{-1} \times\sum_{ij}N_i(|\zeta-E_{ij}|)(dE_{ij}/dx)_0. \tag{12}$$

If we denote the partial energies by $W_{ij}$:

$$W_{ij}=\pm\int_0^{|\zeta-E_{ij}|}EN_i(\omega)d\omega =E_{ij}n_{ij}+\int_0^{|\zeta-E_{ij}|}\omega N_i(\omega)d\omega, \tag{13}$$

then the overlap-hole contribution to the Fermi energy is

$$W_F{}^{\mathrm{II}}=\sum_{ij}W_{ij}. \tag{14}$$

By straightforward differentiation, it is found that

$$(dW_F{}^{\mathrm{II}}/dx)_0=\sum_{ij}n_{ij}(dE_{ij}/dx)_0, \tag{15}$$

which is not zero for the case $x=\xi$; and

$$(d^2W_F{}^{\mathrm{II}}/dx^2)_0=\sum_{ij}n_{ij}(d^2E_{ij}/dx^2)_0 +\sum_{ij}N_i(|\zeta-E_{ij}|)[(d\zeta/dx)_0{}^2-(dE_{ij}/dx)_0{}^2], \tag{16}$$

the last summation differing from Leigh's result only by inclusion of the term $(d\zeta/dx)_0{}^2$. Both $(d\zeta/d\eta)_0$ and $(d\zeta/d\epsilon)_0$ are identically zero. $(d\zeta/d\xi)_0{}^2$ is not zero; hence, it may partially cancel the contribution of the $(dE_{ij}/d\xi)_0{}^2$ in hexagonal metals. In magnesium, however, we find the term, $(d\zeta/d\xi)_0$, rather small. The summations in (14)–(16) are over both overlaps and holes. It is emphasized again that $n_{ij}$ is negative when applied to holes.

In order to obtain numerical results for (15) and (16), it is assumed that during the shear the energies $E_{ij}$ change in the same way as would free-electron energies at the same point in the B.Z.; in other words, the first and second derivatives of $E_{ij}$ are assumed proportional to $E_{ij}$, the constant of proportionality being determined uniquely by the geometry of the B.Z. The results are summarized in Table II for the case of ideal $c/a$ ratio $[c/a=(8/3)^{\frac{1}{2}}]$.

## 5. TEMPERATURE EFFECTS

The previous section represents a straightforward extension of Leigh's theory to crystals of lower than cubic symmetry; it is strictly applicable at absolute zero. At higher temperatures the overlaps and holes are not simply "filled" to the Fermi level $\zeta$, but there is a tailing off which extends to large values of $|E-E_{ij}|$. We expect this temperature effect to be small as long as $|\zeta-E_{ij}|$ is large compared to $kT$ for each overlap and hole. This is not the case, however, for all of the overlaps under consideration, particularly for that one which is initiated in dilute magnesium alloys at an electron-atom ratio of 2.01. Using the experimental value of the density of states (see section 6), it is found that the Fermi level in magnesium alloys is raised by $2.8\times10^{-14}\times\text{erg}\{\sim\frac{2}{3}kT$ at room temperature$\}$ per 0.01 increase in the electron-atom ratio. Thus, it is necessary to extend the results of the last section to finite temperatures in order that the behavior of the elastic constants as a function of alloy composition may be predicted.

If we assume spheroidal energy surfaces, so that $N_i(\omega)=K_i\omega^{\frac{1}{2}}$, then (11) is replaced by

$$n_{ij}=\pm K_i(kT)^{\frac{3}{2}}F_{\frac{1}{2}}(\alpha), \tag{17}$$

where the $+$ and $-$ refer, as before, to overlap and hole, respectively, $\alpha=(\zeta-E_{ij})/kT$ for overlaps, $\alpha=(E_{ij}-\zeta)/kT$ for holes, and $F_n$ is the Fermi-Dirac integral

$$F_n(\alpha)=\int_0^\infty \frac{y^n dy}{\exp(y-\alpha)+1}. \tag{18}$$

TABLE II. First and second derivatives of the various overlap and hole energies in magnesium with respect to the three shear parameters.

| Type | No. of spheroids | $x=\xi$ | $\eta$ | $\epsilon$ |
|---|---|---|---|---|
| | | $(dE_{ij}/dx)_0$ | | |
| $P$ | 2 | $-0.2276\,E_P$ | $-(16/41)\,E_P$ | $0.7169\,E_P$ |
| | 2 | $-0.2276\,E_P$ | $-(16/41)\,E_P$ | $-0.7169\,E_P$ |
| | 2 | $-0.2276\,E_P$ | $(32/41)\,E_P$ | 0 |
| $Q$ | 2 | $-(2/3)\,E_Q$ | 0 | 0 |
| $B$ | 1 | $(4/3)\,E_B$ | 0 | 0 |
| $H$ | 4 | $-0.0206\,E_H$ | $0.0743\,E_H$ | 0 |
| | 2 | $-0.0206\,E_H$ | $-0.1486\,E_H$ | 0 |
| | | $(d^2E_{ij}/dx^2)_0$ | | |
| $P$ | 4 | $0.9648\,E_P$ | $(48/41)\,E_P$ | $(18/41)\,E_P$ |
| | 2 | $0.9648\,E_P$ | 0 | $(18/41)\,E_P$ |
| $Q$ | 2 | $(10/9)\,E_Q$ | $(3/2)\,E_Q$ | 0 |
| $B$ | 1 | $(4/9)\,E_B$ | 0 | $2\,E_B$ |
| $H$ | 4 | $1.3609\,E_H$ | $1.2933\,E_H$ | $0.8360\,E_H$ |
| | 2 | $1.3609\,E_H$ | $0.8959\,E_H$ | $1.4056\,E_H$ |

The properties of these integrals are discussed in a number of places,[12] and tabulated values have been given by McDougall and Stoner.[13] Equation (13) for the energy of each overlap (or hole) is replaced by

$$W_{ij}=E_{ij}n_{ij}+K_i(kT)^{5/2}F_{\frac{3}{2}}(\alpha). \tag{19}$$

Using the new quantities, and proceeding as in Sec. 4, we obtain for the contribution to the elastic constant in place of (16):

$$(d^2W_{\mathrm{F}}^{\mathrm{II}}/dx^2)_0=\sum_{ij}(d^2W_{ij}/dx^2)_0, \tag{20}$$

where

$$\begin{aligned}(d^2W_{ij}/dx^2)_0=n_{ij}(d^2E_{ij}/dx^2)_0&\\ +(d|n_{ij}|/d\mu)[(d\zeta/dx)_0{}^2-(dE_{ij}/dx)_0{}^2]&\\ +[(E_{ij}-\zeta)(d|n_{ij}|/d\mu)+\tfrac{3}{2}n_{ij}]&\\ \times[(d^2\zeta/dx^2)_0-(d^2E_{ij}/dx^2)_0]&\\ +[(E_{ij}-\zeta)(d^2n_{ij}/d\mu)&\\ +\tfrac{1}{2}(d|n_{ij}|/d\mu)](d\zeta/dx-dE_{ij}/dx)_0{}^2;&\end{aligned}$$

$\mu\equiv kT\alpha$. In deriving (20), we have added the term: $-\zeta\sum_{ij}(d^2n_{ij}/dx^2)_0$, which equals zero, just as we did in deriving (16).

The results for zero temperature are adequate for treating pure magnesium, and also for the alloys with the exception of the overlap initiated at 2.01 electrons/atom. Hence, in working out the numerical results of the next section, Eq. (16) was used exclusively, except for this one type of overlap for which $\sum_j(d^2W_{ij}/dx^2)_0$ was computed according to (20).

## 6. COMPARISON WITH EXPERIMENT

In order to obtain numerical values for the shear constants from the theory developed in the previous sections, it is necessary to fix a number of parameters, such as the $E_{ij}$, effective masses, etc. All of the parameters appearing in the equations for the elastic constants may be determined, or estimated, by independent means, with the exception of one unknown (the number of electrons in $P$ overlap positions in pure Mg), which must be obtained from the actual elastic-constant data. The following parameters were determined by the method indicated in parentheses: (a) $\alpha_0$ and all of the $E_{ij}$ (soft x-ray spectrum), (b) total density of states at the Fermi level in pure Mg (electronic specific heat), (c) effective mass of electrons in overlap regions (Hall-effect measurements, or nearly-free electron theory),

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[12] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition.

[13] J. McDougall and E. C. Stoner, Trans. Roy. Soc. (London) **A237**, 67 (1938).

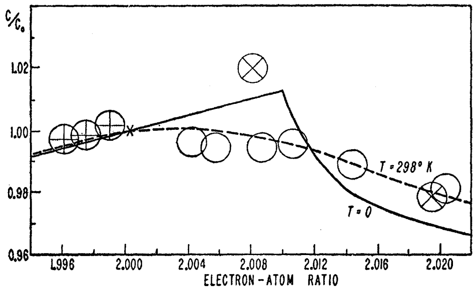

FIG. 3. Behavior of the shear constant $C=c_{11}+c_{12}+2c_{33}-4c_{13}$ as a function of electron-atom ratio in dilute magnesium alloys. The circles represent experimental determinations from alloys with silver, indium, or tin.

and (d) the number of electrons in $B$ overlap positions [from the equations of equilibrium, Eq. (6)]. The Coulomb contribution has already been fixed at 0.50 times the value in Table I.

From measurements of the soft x-ray emission spectrum[14] Mg $L_3$, the width of the full band in magnesium has been estimated to be 6.2 ev. Since the number of overlaps and holes is rather small, all of the values, $E_{ij}$, lie fairly close to this number. The actual values used, $E_B=E_P=5.75$ ev, $E_H=6.5$ ev, cannot be very much in error. But $E_H$ is the high point in the B.Z.; hence, the value $E_H=6.5$ ev may be used to calculate $\alpha_0$. On the assumption of free electronlike behavior right to the boundary of the B.Z., $\alpha_0=0.73$; but for $E(\mathbf{k})$ curves of the form (7) with $\lambda\neq 0$, $\alpha_0$ is larger. We have chosen $\alpha_0=0.85$.

As mentioned in Sec. 2, the crystal must be in equilibrium with respect to the various shears, and in particular, Eq. (6) must hold. Two of the first derivatives, those with respect to $\eta$ and $\epsilon$, vanish identically, but the condition that $(dW/d\xi)_0=0$ must be imposed. At the ideal $c/a$ ratio $(dW_{\text{Coul}}/d\xi)_0=0$, and $(dW_F{}^{\text{I}}/d\xi)_0=-15.3\times 10^9$ erg cm$^{-3}$; at the observed $c/a$ ratio of magnesium, there is an *additional* contribution (Coulomb plus full-zone) $=+2.7\times 10^9$ ergs cm$^{-3}$. Hence $(dW_F{}^{\text{II}}/d\xi)_0$, given by (15), is

$$(dW_F{}^{\text{II}}/d\xi)_0=12.6\times 10^9 \text{ ergs/cm}^3. \tag{21}$$

The interesting result is that the number in (21) is positive; hence, overlaps or holes with a positive $n_{ij}(dE_{ij}/d\xi)_0$ must dominate. A glance at Table II shows us that $B$ overlaps must be present in pure magnesium, a result which is at variance with the usual assumptions for this metal. We cannot fit all of the elastic-constant data, however, with only $B$-type overlaps. For the second type we have chosen $P$ overlaps. If $p$ denotes the ratio of total $P$-type electrons per unit volume to total $B$-type electrons per unit volume ($n_B$), then from (15) and (21):

$$n_B[(4/3)E_B-0.2276pE_P+0.0206(1+p)E_H] =12.6\times 10^9 \text{ ergs/cm}^3. \tag{22}$$

Equation (22) provides a relationship between $n_B$ and $p$, but in practice, it essentially determines $n_B$ since $p$ is of the order of one.

Measurements of the electronic specific heat[15,16] give the total density of states per unit energy range at the Fermi level in pure Mg, i.e., $\sum_{ij} N_i(\zeta-E_{ij})$, equal to $15.3\times 10^{33}$ erg$^{-1}$ cm$^{-3}$. Essentially the same number is obtained from the magnetic susceptibility.[17] Now each of the overlaps is small, so we may approximate the effective mass from nearly-free-electron theory:

$$(m^*/m)=(1+4E_c/\Delta E)^{-\frac{1}{2}} \tag{23}$$

where $E_c$ is the energy at the midpoint of the gap and $\Delta E$ is the gap width. Using the results of Trlifaj's calculation[18] for magnesium, we estimate $(m^*/m)$ for the $B$ overlap to be 0.40. We can estimate $(m^*/m)_{\text{overlap}}$ in yet another way, from the conductivity and Hall coefficient[6] of the pure metal. Now the total number of overlap electrons is of the order of $10^{21}$ cm$^{-3}$ (see Table III),† so that in order for the Hall coefficient to be as small as it is, there must be almost complete cancellation between the overlap and hole terms. Characterizing the overlaps with the mobility $u_1$ and the holes with $u_2$, then $u_1\approx u_2$. If we assume that the relaxation time $\tau$ is the same for overlaps and holes, then $m_1{}^*\approx m_2{}^*$. Combining this result with Eq. (22) using an approximate value for $p$, we obtain $(m^*/m)_{\text{overlap}}=0.7$. The two methods are about equally reliable; hence, about the best we can do is to take a simple average of the two values, namely, $(m^*/m)_{\text{overlap}}=0.55$.

The value of $p$ is still undetermined. Choosing it in such a way as to obtain the best fit to the elastic

TABLE III. Quantities used in Eq. (16) to determine the elastic constants.[a]

| Quantity | Value |
|---|---|
| $E_B$, $E_P$ | 5.75 ev |
| $E_H$ | 6.5 ev |
| $\alpha_0$ | 0.85 |
| Coulomb factor[b] | 0.45 |
| $n_B$ | $1.10\times 10^{21}$ cm$^{-3}$ |
| $6n_P$ | $0.60\times 10^{21}$ cm$^{-3}$ |
| $6n_H$ | $1.70\times 10^{21}$ cm$^{-3}$ |
| $N_B$ | $1.46\times 10^{33}$ erg$^{-1}$ cm$^{-3}$ |
| $6N_P$ | $3.95\times 10^{33}$ erg$^{-1}$ cm$^{-3}$ |
| $6N_H$ | $9.94\times 10^{33}$ erg$^{-1}$ cm$^{-3}$ |
| $(m^*/m)_B$, $(m^*/m)_P$ | 0.55 |
| $(m^*/m)_H$ | 0.98 |

[a] $n_p$ is the number associated with one of the six spheroids of this type.
[b] The value 0.45, instead of 0.5, gave improved agreement with all of the experimental data; hence, this multiplicative factor was used.

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[14] H. W. B. Skinner, Trans. Roy. Soc. (London) **A239**, 95 (1940).

[15] C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 233.

[16] P. L. Smith, Phil. Mag. **46**, 744 (1955).

[17] See reference 12, p. 157.

[18] M. Trlifaj, Czechoslav. J. Phys. **1**, 110 (1952).

† The values of $E_B$, $E_P$, and $E_H$ as given in Table III are only approximate in that they have not been carried to the limit of self-consistency with other parameters in the table. It is evident from the values of $n_B$ and $n_P$ that $E_P$ is several tenths ev larger than $E_B$.

constant data, $p = 0.55$. Equation (22) then gives $n_B = 1.10 \times 10^{21}$ cm$^{-3}$.

The contributions to the elastic shear constants, $C$ and $C'$, of pure magnesium are given in Table IV, whereas the changes in $C$, $C'$, and $c_{44}$ per 0.01 increase in the electron-atom ratio (on the assumption that no new overlap types are initiated) are presented in Table V. The value of $c_{44}$ in pure Mg could not be compared because, as mentioned in Sec. 4, the full-zone contribution to this constant was not determined. The full-zone term does not change with alloying, however; hence, the dependence of $c_{44}$ on electron-atom ratio is readily computed.

TABLE IV. Contributions to the elastic shear constants of pure magnesium in units of $10^{12}$ dynes/cm$^2$.

| | $C$ | $\frac{1}{2}(c_{11}-c_{12})$ |
|---|---|---|
| Coulomb term | 1.148 | 0.135 |
| Full zone term | 1.194 | 0.163 |
| Overlap-hole term | −1.116 | −0.130 |
| Total | 1.226 | 0.168 |
| Experiment[a] | 1.226 | 0.168 |

[a] See references 2–4.

Just as in the aluminum case, we find also in magnesium a negative contribution from the overlap-hole term, arising primarily from the second summation in (16). The overlap-hole term in $C$ is due primarily to $B$ overlaps, in $C'$ is due primarily to $P$-type overlaps. On the other hand, the hexagonal metals, zinc and cadmium, with larger $c/a$ ratios, presumedly do not have $P$-type overlaps; hence, the overlap-hole term in $C'$ would be quite small. We believe this is the explanation for the fact that $C'$ is so much larger relative to $C$ in these metals.

The change in the $n_{ij}$ due to alloying produces a corresponding change in the contribution (15) to the first derivative with respect to $\xi$. This change must be compensated by a change in both $(dW_F{}^I/d\xi)_0$ and $(dW_{\mathrm{Coul}}/d\xi)_0$, implying a change in $c/a$. Unfortunately, this predicted change in $c/a$ cannot be compared directly with experiment, since there are also changes in volume and associated changes in the $E_{ij}$ due to alloying, and these volume changes are much larger than the changes in $c/a$.

TABLE V. Change in the shear constants of dilute magnesium alloys per 0.01 increase of the electron-atom ratio (in units of $10^{12}$ dynes/cm$^2$).

| | $C$ | $C'$ | $c_{44}$ |
|---|---|---|---|
| Δ overlap-hole | 0.0052 | −0.00145 | −0.00295 |
| Δ Coulomb | 0.0112 | 0.00135 | 0.00074 |
| Total | 0.0164 | −0.0001 | −0.00221 |
| Experiment[a] | (see Fig. 3) | −0.0008<br>±0.0008 | −0.0015<br>±0.0006 |

[a] See reference 4.

Finally we must comment about the new type of overlap initiated at an electron-atom ratio of 2.01. Since we require both $B$- and $P$-type overlaps in the pure metal, the new overlap must be of $Q$ type. Now, the important contribution from a new overlap to the elastic constant is from the first derivative term, and a glance at Table II shows that $C'$ and $c_{44}$ will be unaffected. The shear constant $C$, on the other hand, will show an abrupt decrease of the type predicted by Leigh. This abrupt decrease, superposed on the rising trend given in Table V, and plotted in Fig. 3, is characteristic of the behavior at absolute zero; the room temperature curve, obtained by using Eq. (20) for the $Q$ type overlaps, evaluating the derivatives from the McDougall and Stoner tables,[13] is much more gradual and appears to agree rather well with the experimental data.

It seems that a repetition of the measurements of Long and Smith[4] at lower temperatures might be in order. The scatter in their data appears to be small enough that the break in the curve ought to be quite apparent even at liquid nitrogen temperatures.