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Elastic Constants of Magnesium-Lithium Alloys

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The elastic constants of single crystals of magnesium and of dilute alloys of magnesium with lithium have been measured at 298°K using the pulse-echo technique. The alloys covered the range of 1.841–2.0 electrons per atom. All fundamental elastic constants decrease with increasing lithium content. In terms of $C_0^{-1}(dC/dx)$ the values are c_{44}, (-0.411); $\frac{1}{2}(c_{11}-c_{12})$, (-0.235); $c_{11}+c_{12}+2c_{33}-4c_{13}$, (-0.400) per atom fraction of lithium. These values are corrected for the change in lattice parameter upon alloying by using experimental data on the pressure derivatives of the elastic constants of pure magnesium. The remaining effect is due to alloying alone (change in the electron-atom ratio) and is still negative for all three shear constants. In terms of $C_0^{-1}(\partial C/\partial x)_{v,\,c/a}$ the values are c_{44}, (-0.827); $\frac{1}{2}(c_{11}-c_{12})$, (-0.589); $c_{11}+c_{12}+2c_{33}-4c_{13}$, (-0.886) per atom fraction of lithium. These results may be interpreted as indicating, first, a decrease in the long-range electrostatic forces because of the decrease in the average ion-core charge, and second, a decrease in the Fermi stiffness. The decrease in the Fermi stiffness is attributed to: (1) an increase in the volume of electron holes—a hole contributes negatively to the Fermi stiffness—and a decrease in the volume of the overlap electrons in the Brillouin-zone structure with decreasing electron-atom ratio; (2) the transfer (under shear) of electrons from those faces receding from the origin of the Brillouin zone to those approaching it. The over-all effect of this transfer phenomenon is also to decrease the Fermi stiffness.

INTRODUCTION

MAGNESIUM has a hexagonal close-packed (hcp) structure with a c/a ratio, extrapolated to 0°K, of 1.624 which is very close to the perfect packing ratio of 1.633. It is divalent and has two atoms per unit cell. Therefore it has just enough electrons to completely fill the first and second Brillouin zones (BZ). However, since the conduction electrons in magnesium are not tightly bound the first double zone has regions (holes) not occupied by electrons, whereas electrons occupy some volume in the third and fourth zones (electron overlaps). In pure magnesium, the volumes of the holes and overlaps are equal. However, in alloys where the hcp structure of magnesium is preserved (as in dilute magnesium-lithium alloys), the volumes of the holes and overlaps depend on the electron-atom ratio. The BZ structure of pure magnesium and of dilute magnesium alloys has been the subject of many theoretical and experimental studies with varying results. Most experimental work has dealt with the effect of alloying upon the lattice constant a, the axial ratio c/a, and the elastic constants of single crystals, c_{11}, c_{12}, etc. The variations of lattice spacing of magnesium solid solutions with the amount and type of solute was studied by Hume-Rothery and Raynor,[1] Raynor,[2] Busk,[3] von Batchelder and Raeuchle,[4] and Hardie and Parkins.[5] Raynor observed that the variations of lattice spacing with percent solute (metals having a higher valency than magnesium) in dilute magnesium alloys exhibited a discontinuity at electron-atom ratios e/A near 2.01. He attributed the discontinuity to new BZ overlaps across the Brillouin planes that are perpendicular to the c axis, brought about by increasing the electron-atom ratio. However, von Batchelder and Raeuchle, using a large number of magnesium alloys, observed no such discontinuity in the case of aluminum. Only a negligible discontinuity was observed in indium-magnesium alloys. They concluded that BZ overlap does not necessarily result in axial-ratio anomalies. Furthermore, Hardie and Parkins,[6] using uni-, bi-, ter-, quadri-, and quinquevalent solutes, also failed to observe the discontinuities reported by Raynor. It has been suggested by von Batchelder and Raeuchle that the anomaly observed by Raynor was due to short-range ordering. The results of Hardie and Parkins suggested that in magnesium alloys the spacing of the solid solution lattice depends on size effects, being completely independent of the solute valency, whereas the axial ratio c/a is determined by the electron concentration. In fact, they describe their data by

$$c/a=1.50319+0.060085E\,\text{Å}\,, \tag{1}$$

where E is the electron concentration based on the normal group valencies associated with the solutes concerned. Salkovitz *et al.*[7] reported anomalies in the thermoelectric power of magnesium-cadmium alloys which they ascribed to overlap effects. In most cases, however, these anomalies were observed at e/A ratios different from those reported by Raynor. Rayne[8] reported on the heat capacity of dilute magnesium-aluminum alloys. From the observed variations of the electronic contributions which are a function of the

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[1] W. Hume-Rothery and G. V. Raynor, J. Inst. Metals **63**, 227 (1938).

[2] G. V. Raynor, Proc. Roy. Soc. (London) **A174**, 457 (1940).

[3] R. S. Busk, Trans. AIME **188**, 1460 (1950).

[4] F. W. von Batchelder and Raeuchle, Phys. Rev. **105**, 59 (1957).

[5] D. Hardie and R. N. Parkins, J. Inst. Metals **85**, 449 (1957).

[6] D. Hardie and R. N. Parkins, Phil. Mag. **4**, 815 (1959).

[7] E. I. Salkovitz, A. E. Shindler, and E. W. Kammer, Phys. Rev. **105**, 887 (1957).

[8] J. Rayne, J. Phys. Chem. Solids **7**, 268 (1958).

density of states with increasing e/A ratio, he concluded that an overlap of the kind suggested by Raynor is initiated at an e/A ratio of about 2.02.

A slight change in the lattice spacing and of the axial ratio c/a of a hexagonal metal produces a large change in the elastic constants of its single crystals. Hence the variation of the elastic constants of magnesium single crystals with alloying may provide a more sensitive measure (than that provided by investigations of lattice parameter, thermoelectric power, or heat capacity) of the initiation of new electron overlap in magnesium solid solutions with increasing e/A ratio, or of the removal of some already existing overlaps with decreasing e/A.

In the method of Leigh[9] for the calculation of the electronic contributions to the elastic shear constants of metals which have a nearly filled zone and an electron overlap into the next higher zone, two contributions are recognized: an electrostatic term and a Fermi term. The Fermi term may be divided into two parts: a full-zone term and an overlap-hole term. The full-zone calculation assumes that the Brillouin zone is fully occupied, allowing for energy changes through the movement of the Brillouin-zone planes. Such movement can be brought about through a change of the lattice parameters. The overlap-hole term, 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. When such transfer occurs in a metal under the action of shear strain, the overlap-hole contribution to the elastic shear constants will be negative in sign while the electrostatic and the full-zone terms are positive. Therefore, alloying of such metals with solutes that bring about an increase (decrease) in the volume of the holes and a decrease (increase) in the volume of the overlaps (all other factors being constant) should result in a decrease (increase) in the elastic shear constants.

This paper reports on the effect of alloying magnesium with lithium, in the range of e/A between 2.0 and 1.84, upon the elastic constants of solid-solution single crystals at room temperature. The experimental determination of the elastic constants was made using the pulse-echo technique.

EXPERIMENTAL PROCEDURE

Single-crystal spheres 2.5 cm in diameter were prepared from high-purity magnesium, supplied through the courtesy of the Dow Chemical Company. The spheres were grown by directional solidification in a graphite mold under an argon atmosphere using a modified Bridgman technique. The spheres, oriented by the Laue back-reflection technique, were used to seed 1.5-cm-diam cylindrical crystals of pure magnesium. Some of the seeds were grown from the basal plane—which then lies in the end faces of the cylindrical crystals. Others were grown at 90° to the basal plane, the c axis lying in the end faces. The crystals of these two orientations were then cut by an acid saw into cylinders 2.5 cm in length and were used as seeds for the magnesium-lithium single crystals.

Two 1.5-cm round extruded rods of each magnesium-lithium alloy to be investigated were seeded from the two previously described types of magnesium seeds. Because of the chemical activity of lithium, the alloy crystals were grown under an argon atmosphere in a split steel mold (AISI 1020) having a 10-cm solid-steel heat sink below the seed to produce a steep temperature gradient across the interface. The solid-to-liquid interface traversed the length of the 1.5-cm section at a rate of 0.6 cm per h. After the alloy had solidified, it was carefully removed from the mold. The 1.5-cm-diam test section of the single crystal was acid cut to a length of 9 cm by removing the seed and the 2.5-cm-diam reservoir section.

Magnesium can dissolve up to 16 at.% lithium in the hcp structure. The phase diagram[10] indicates that the liquidus and solidus curves separate slightly, which suggests that dilute alloys (less than 5 at.% lithium) could be handled similarly to pure magnesium. For the alloys with lithium content up to 16 at.%, care must be taken so that minimum variation in composition with length of the grown cylinders is attained. This is accomplished by using a 5-cm reservoir section on the crystal blank; the crystal itself is then only about $\frac{1}{8}$ of the total weight of the alloy. Thus when the crystal proper has solidified, only $\frac{1}{8}$ of the total melt has been removed, and the composition gradient over the gauge length is kept to less than 0.5 at.%. The composition gradient of the crystals of each alloy were obtained by flame photometry.

The crystal end faces were carefully machined flat for smooth contact with the transducers. They were then annealed in an argon atmosphere for 15 min at 773°K to remove any cold work. The remaining degree of cold work was negligible, as was evident from the shape of the acoustic pulse at the leading edge, where forerunners were almost absent. The precise crystallographic orientation of the acoustic faces was determined from back-reflection Laue photographs. We observed no significant rotation of the c axis in one face relative to the other (such as was observed by Eros and Smith[11]). Perhaps this was so because we succeeded in minimizing the concentration gradient along the crystal length. Seven alloy single crystals of each orientation in the range 1.5 to 16 at.% lithium, in addition to two single crystals of pure magnesium, were prepared using the method outlined above.

Magnesium has five independent elastic constants: c_{11}, c_{12}, c_{13}, c_{33}, and c_{44}. Three of the elastic constants

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

[10] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed.

[11] S. Eros and C. S. Smith, Acta Met. **9**, 14 (1961).

TABLE I. The adiabatic elastic constants of pure magnesium and magnesium-lithium alloys at 298°K. Results are expressed in units of 10^{12} dyn cm^{-2}.

Li concentration (at.%)	Electron-atom ratio	c_{11}	c_{12}	C'	c_{44}	$\mathcal{C}$	c_{33}	c_{13}
0	2.0	0.5950	0.2612	0.1669	0.1635	1.215	0.6155	0.2180
1.51	1.985	0.5924	0.2600	0.1662	0.1625	1.2075	0.6128	0.2176
3.02	1.970	0.5892	0.2588	0.1652	0.1614	1.2010	0.6095	0.2165
5.10	1.949	0.5853	0.2572	0.16406	0.1601	1.1901	0.6055	0.2158
7.0	1.930	0.5795	0.2539	0.16281	0.1587	1.1816	0.5994	0.2126
10.0	1.900	0.5724	0.2510	0.1607	0.1568	1.1664	0.5921	0.2103
12.05	1.880	0.5672	0.2479	0.15963	0.1555	1.1581	0.5868	0.2076
14.15	1.859	0.5627	0.2464	0.15813	0.1539	1.1466	0.5821	0.2067
15.94	1.841	0.5549	0.2415	0.1567	0.1525	1.1361	0.5742	0.2022

may be taken as pure shears. A common and convenient set is

$$\begin{aligned}&\mathcal{C}=c_{11}+c_{12}+2c_{33}-4c_{13},\\&C'=\tfrac{1}{2}(c_{11}-c_{12}),\qquad (2)\\&c_{44}.\end{aligned}$$

The constant $\mathcal{C}$ corresponds to a strain ϵ that changes the c/a ratio at constant volume, leaving the symmetry of the crystal unchanged. The constant C' corresponds to a strain γ which changes the angle between any pair of axes in the basal plane, leaving the c axis unaffected. The c_{44} constant corresponds to a strain δ which tilts the c axis with respect to the basal plane.

These shear constants are obtained from the crystal binding energy E by taking the second derivatives with respect to the appropriate strain:

$$\tfrac{1}{2}\partial^2E/\partial\epsilon^2=\Omega\mathcal{C},\qquad (3)$$

$$\tfrac{1}{2}\partial^2E/\partial\gamma^2=\Omega C',\qquad (4)$$

$$\tfrac{1}{2}\partial^2E/\partial\delta^2=\Omega c_{44},\qquad (5)$$

where the X axis is taken along the direction of propagation. V_1, V_2, and V_3 are the velocities of a longitudinal wave and two shear waves propagated along the X axis, respectively. Hence a longitudinal wave propagated in the basal plane determines c_{11}, a shear wave propagated in the basal plane with particle motion in the basal plane determines $\frac{1}{2}(c_{11}-c_{12})$, and a shear wave with particle motion along the c axis determines c_{44}. Thus, a pair of plane parallel faces which contain the c axis can be used to measure these three constants.

To measure c_{13} and c_{33}, another pair of plane parallel faces which contain the basal plane are used. V_1 and V_3 taken together determine c_{33}, and either V_1 or V_3 then allows a determination of c_{13}.

The apparatus described in Refs. 11 and 12 was used in measuring the transit times of the various acoustic waves. A pulse of 0.2-μsec duration was used to drive a 10-Mc/sec quartz transducer.

The quartz-sample seal used was a Dow Corning silicone oil, DC-200 (1000 cS). All measurements were made in air at room temperature, 25.0±0.4°C.

RESULTS

The elastic constants of the pure magnesium and the magnesium-lithium alloy single crystals as measured in this present investigation are listed in Table I. The results are self-consistent. A comparison of the values of pure magnesium given in Table I with literature values is given in Table II. Table III gives the values of the ratio C/C_0 for the three shear constants $\mathcal{C}$, C', and c_{44}. Here C_0 is the value of the corresponding constant for

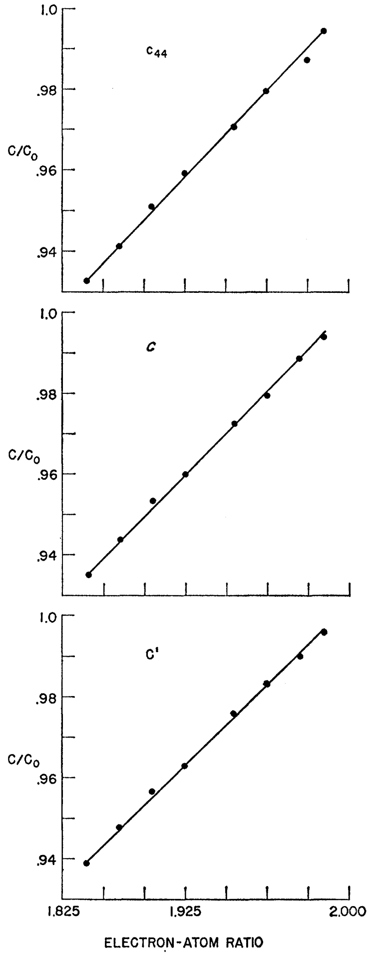

FIG. 1. The elastic constants c_{44}, C', and $\mathcal{C}$ of Mg-Li alloys, normalized to those of pure magnesium, versus electron-atom ratio.

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[12] S. Eros and J. R. Reitz, J. Appl. Phys. 29, 683 (1958).

TABLE II. The adiabatic elastic constants of pure magnesium at 298°K compared with those obtained by other investigators. Entries are in units of 10^{12} dyn cm^{-2}.

Experiments	Temp. (°K)	c_{11}	c_{12}	c_{13}	c_{33}	c_{44}	C'	$\mathcal{C}$
Present	298	0.5950	0.2612	0.21805	0.6155	0.1635	0.1668	1.215
[a]	298	0.5969	0.2622	0.217	0.616	0.1638	0.1674	1.223
[b]	298	0.5905	0.2545	0.2130	0.6125	0.1632	0.1680	1.218
Ref. 11	298	0.5928	0.2590	0.2157	0.6135	0.1632	0.1669	1.216

[a] T. R. Long and C. S. Smith, Acta Met. **5**, 200 (1957).
[b] L. J. Slutsky and C. W. Garland, Phys. Rev. **107**, 97 (1957).

pure magnesium. A plot of normalized shear constants versus the electron-to-atom ratio e/A is shown in Fig. 1.

TABLE III. The shear constants of magnesium-lithium alloys normalized to their value in pure magnesium, 298°K. The elastic constants are in units of 10^{12} dyn cm^{-2}.

Li concentration (at.%)	Electron-atom ratio	$\mathcal{C}$	C'	c_{44}
1.51	1.985	0.9938	0.9958	0.9939
3.02	1.970	0.9885	0.9898	0.9871
5.10	1.949	0.9795	0.9829	0.9792
7.0	1.930	0.9725	0.9755	0.9706
10.0	1.900	0.9600	0.9628	0.9590
12.05	1.880	0.9532	0.9564	0.9511
14.15	1.859	0.9437	0.9474	0.9413
15.94	1.841	0.9351	0.9389	0.9327

DISCUSSION

A significant fraction of the total change in the elastic constants upon alloying arises from the change in lattice parameter, or volume. For the purpose of interpretation in microscopic terms, it is necessary to know the change which a solute atom would produce at constant lattice parameter (in cubic systems) or at constant volume (e.g., in hexagonal systems). Hence a correction for the change of the elastic constant with volume is needed. Such a correction may be determined theoretically.[13–15] However, this requires a knowledge of the microscopic model which is often the object of the investigation. The pressure derivative of an elastic constant dC/dP, however, permits one to compute immediately the quantity $(\partial C/\partial \ln v)_{x,c/a}$, the change of the elastic constant C with volume v at constant composition x and c/a ratio. In magnesium the strain produced by hydrostatic pressure is almost a pure dilation, so that the measured pressure derivatives yield good numbers for the change of the elastic constants with volume. If the elastic constant C is taken to be a function of volume v, axis ratio c/a, and composition x (as in a hexagonal system, for example), then the total variation of C at constant temperature is

$$dC/dx=(\partial C/\partial x)_{v,c/a}+(\partial C/\partial \ln v)_{x,c/a}(d\ln v/dx)\\ +(\partial C/\partial \ln(c/a))_{x,v}(d\ln(c/a)/dx).$$

According to Hardie and Parkins,[6] the addition of lithium solute into magnesium produces primarily a volume change. The magnitude of $d\ln v/dx$ is approximately nine times as large as $d\ln(c/a)/dx$ (Table V). Therefore, Eq. (9) may then be approximated by

$$dC/dx=(\partial C/\partial x)_{v,c/a}\\ +(\partial C/\partial \ln v)_{x,c/a}(2d\ln a+d\ln c)/dx,\quad (6)$$

where $d\ln v/dx=(2d\ln a+d\ln c)/dx$.

At constant temperature, composition, and c/a ratio, the variation of the shear constant C with volume is related to its pressure derivative by[16]

$$(\partial C/\partial \ln v)_{x,c/a}=-B_T(dC/dP).\quad (7)$$

The pressure derivatives of the elastic constants of magnesium have been determined by Schmunk and Smith.[16] Their values of dC/dP for the various shear constants, Table IV, and the data of Hardie and Parkins on the effect of lithium alloying upon the lattice parameter of magnesium, Table V, are used to evaluate the correction term to the elastic constant due to a change in volume upon alloying. The details of this correction are shown in Table VI. It is observed that the quantity

$$(1/C_0)(\partial C/\partial x)_{v,c/a}$$

is still negative for all three shear constants.

A discussion of the variation of the shear constants with composition, $(\partial C/\partial x)_{v,c/a}$, is of primary interest here. This requires a consideration of the various constituents of the elastic constants. The important contributions to the elastic constants are (1) the long-range electrostatic stiffness C_E which arises from the change, upon straining, in the electrostatic energy of the positive ions immersed in a negative uniform sea of electrons—

TABLE IV. Pressure derivatives of the elastic stiffnesses of magnesium at 25°C according to Schmunk and Smith (Ref. 16).

	c_{44}	C'	$\mathcal{C}$	Units
dC/dP	1.58	1.36	13.7	...
B_T			0.343	10^{12} dyn/cm^2
$-B_T(dC/dP)$ $=(\partial C/\partial \ln v)_{x,c/a}$	0.542	0.466	4.70	10^{12} dyn/cm^2

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[13] C. S. Smith and J. W. Burns, J. Appl. Phys. **24**, 15 (1953).
[14] J. R. Neighbours and C. S. Smith, Acta Met. **2**, 591 (1954).
[15] R. Bacon and C. S. Smith, Acta Met. **4**, 337 (1956).
[16] R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids **9**, 100 (1959).

TABLE V. Magnesium lattice parameters and their variation with percent lithium solute at 298°K according to Hardie and Parkins (Ref. 6).

Solute	Atomic %	c (Å)	a (Å)	c/a	dc/dx (10^{-4} Å/at.%)	da/dx (10^{-4} Å/at.%)	$d(c/a)/dx$ (10^{-4} Å/at.%)	$\dfrac{d\ln(c/a)}{dx}$ (10^{-4} per at.%)	$d\ln v/dx$ (10^{-4} per at.%)
Mg	...	5.2108	3.2099	1.6234	...	...	...	...	...
Li	1.03	5.2073	3.2089	1.6228	−35.7	−9.2	−2.3	−1.418	−12.58
	4.66	5.2011	3.2071	1.6218					
	9.93	5.1759	3.2008	1.6171					
	14.03	5.1702	3.1994	1.6160					

this term is a positive contribution to the elastic stiffnesses; (2) a term C_I due to the change in the short-range repulsive interaction between closed-shell ion cores, which is also a positive contribution; (3) a term C_F due to the change in the Fermi energy of the electrons caused by movements of the Brillouin-zone planes as the metal is sheared. The Fermi term C_F may be divided into two parts: a full-zone term which is positive, and an overlap-hole term which is negative in sign.

The stiffness C_I, which is due to short-range repulsion between ion cores, is sharply dependent on the amount of nearest-neighbor ion-core overlap. The change in the ion-core stiffness upon alloying is then expected, for dilute alloys, to be proportional to the atomic solute fraction Δx:

$$(C_I)_{\text{alloy}}=C_{I0}(1+\alpha\Delta x)\,, \tag{8}$$

where the subscript 0 refers to pure magnesium.

The coefficient α, which should be a constant for a particular solute, is a function of two parameters: the ion radius and the electronic charge of the closed-shell ion of the solute. If the electronic charge of the closed-shell ion cores is the same for both solvent and solute, then α is positive if the ion radius of the solute is larger that that of the matrix atom. Similarly, if the ionic radii of solvent and solute are equal, then α is positive when the electronic charge on the closed-shell ion of the solute is larger than that of the solvent and conversely. However, since the ion cores in magnesium are rather small (ion radius = 0.65 Å) and are well separated (nearest-neighbor distance = 3.19 Å), it is expected that the C_{I0} contribution to the total elastic stiffness in pure magnesium will be rather small. In fact, direct calculation by Huntington[17] has indicated that the short-range repulsion between ion cores contributes at most a few percent to each shear constant in magnesium. Furthermore, since the ion cores in lithium are equally small (ion radius = 0.68 Å), the ion-core stiffness in the dilute magnesium-lithium alloys is equally small. Therefore, the exact variation of the ion-core repulsion term of the dilute alloys with solute concentration is not very critical and may be assumed well represented by Eq. (8).

Various quantitative treatments of the Fermi contribution to the elastic stiffness of magnesium have been attempted. In these attempts, it is noted that because of the complexity of the problem, many almost arbitrary assumptions are invoked and many of the parameters involved are often arbitrarily modified to explain some particular data. It is therefore sufficient at this time to account for the variation of the total Fermi stiffness C_F with composition simply by assuming that the Fermi stiffness of the alloy is equal to that of pure magnesium multiplied by a factor N which is expected to be close to unity for the dilute alloys.

The long-range electrostatic stiffness depends on the square of the net ion charge. It is hence assumed that the electrostatic stiffness for the alloy is equal to that of pure magnesium multiplied by a parameter Z^2 which is also expected to be near unity for the dilute alloys. The shear constants for the alloy will thus be given by

$$C=C_{I0}(1+\alpha\Delta x)+C_{F0}N+C_{E0}Z^2\,. \tag{9}$$

The coefficients of α, N, and Z^2 are the values for pure magnesium, Table VII. If we subtract from Eq.

TABLE VI. Lattice-parameter correction for Mg-Li alloys at 298°K. The composition is expressed as at.% of lithium.

		c_{44}	C'	$\mathfrak{C}$
Total change	$(1/C_0)dC/dx$	-4.107×10^{-3}/at.%	-2.35×10^{-3}/at.%	$-4\ \times10^{-3}$/at.%
Ref. 16	$(1/C_0)(\partial C/\partial\ln v)_{x,c/a}$	−3.32	−2.82	−3.87
Ref. 6	$d\ln v/dx$	-12.58×10^{-4}/at.%	-12.58×10^{-4}/at.%	-12.58×10^{-4}/at.%
Correction for lattice-parameter change	$(1/C_0)(\partial C/\partial\ln v)\times(d\ln v/dx)$	4.170×10^{-3}/at.%	3.54×10^{-3}/at.%	4.86×10^{-3}/at.%
Change due to alloying	$(1/C_0)(\partial C/\partial x)_{v,c/a}$	-8.27×10^{-3}/at.%	-5.89×10^{-3}/at.%	-8.86×10^{-3}/at.%

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[17] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

TABLE VII. Contributions to the elastic shear constants of pure magnesium in units of 10^{12} dyn cm^{-2}.

Term	$\mathcal{C}$	C'	c_{44}
Coulomb,[a] C_{E0}	1.139	0.135	0.145
Ion core,[a] C_{I0}	0.468	0.057	0.033
$C_{E0}+C_{I0}$	1.607	0.1920	0.178
Observed,[b] $C_{\mathrm{ob.}}$	1.346	0.1863	0.1830
Fermi $C_{F0}=C_{\mathrm{ob.}}-C_{E0}-C_{I0}$	-0.261	-0.006	0.005

[a] According to the method of Huntington (Ref. 17) with $n^2=1.8$.
[b] L. J. Slutsky and C. W. Garland, Phys. Rev. **107**, 97 (1957).

(9) the constants for pure magnesium C_0 and then divide by C_0 and by the solute atomic fraction Δx, we obtain the fractional change in $\mathcal{C}$, c_{44}, and C' per atom fraction solute,

$$\frac{1}{\mathcal{C}_0}\left(\frac{\Delta\mathcal{C}}{\Delta x}\right)=0.0349\frac{\alpha}{\Delta x}+0.119\frac{N-1}{\Delta x}+0.8462\frac{Z^2-1}{\Delta x}, \tag{10a}$$

$$\frac{1}{(c_{44})_0}\left(\frac{\Delta c_{44}}{\Delta x}\right)=0.0180\frac{\alpha}{\Delta x}+0.191\frac{N-1}{\Delta x}+0.792\frac{Z^2-1}{\Delta x}, \tag{10b}$$

$$\frac{1}{C_0'}\frac{\Delta C'}{\Delta x}=0.0306\frac{\alpha}{\Delta x}+0.245\frac{N-1}{\Delta x}+0.7258\frac{Z^2-1}{\Delta x}. \tag{10c}$$

The difference $(1/C_0)(\Delta C/\Delta x)$ is replaced by $(1/C_0)\times(\partial C/\partial x)_{v,c/a}$, and its value from Table VI is substituted in the above equations. The resulting expressions are then solved simultaneously for α, N, and Z^2; we obtain

$$\alpha=0.58, \tag{11a}$$

$$N=1+2.309\Delta x, \tag{11b}$$

$$Z^2=1-1.61\Delta x, \tag{11c}$$

describing the behavior of the elastic shear constants of Mg-Li alloys.

The Coulomb contribution to the shear constant C_E has been computed by Huntington[17] by means of the Ewald method on the assumption that the doubly charged ion cores move in an electron sea of uniform density. His results may simply be represented by

$$C_E=K(ne)^2,$$

where K is a constant for a particular shear constant, e is the electronic charge, and n is the number of charges on an ion. A value of $n=2$ for magnesium would represent the maximum Coulomb contributions. However, (1) nonuniform electron density (the actual charge density at the boundary of the atomic polyhedron is different from the value which one would get if the charge were distributed uniformly over the volume of the atomic cell), (2) relaxation effects predicted by Zener[18] and Huntington, and (3) the fact that magnesium is not completely ionized, all serve to reduce the magnitude of the Coulomb term appreciably. The electrostatic contribution used by Reitz and Smith[19] corresponds to an n^2 value of 1.8 in magnesium. Calculations by Brooks[20] based on the quantum defect method yield a value of 1.15 for n^2 in lithium. Therefore, the Coulomb term C_E should decrease with increasing lithium content, in agreement with Eq. (11c).

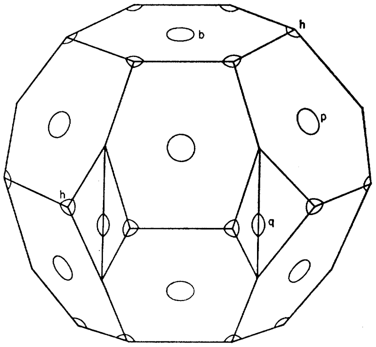

FIG. 2. The Brillouin zone of magnesium, showing the positions of electron overlaps b, p, and q and of holes h.

The resulting $\alpha>0$ simply indicates that the increase in C_I due to added nearest-neighbor ion-core overlap resulting from alloying magnesium with lithium is more than sufficient to offset the decrease in C_I due to the drop in the average ion-core charge.

As previously stated, the conduction electrons in magnesium are not localized; therefore, the first double zone has electron holes, whereas the third and fourth zones contain electron overlaps. An early model of the BZ is shown in Fig. 2.

The positions of the holes are denoted by the symbol h. The electron overlap positions are more speculative, since there are a number of possibilities. On the nearly-free-electron model one would have several 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. It is clear from the figure that the maximum possible numbers of overlaps are two of the b type, twelve of the p type, and four of the q type.

In extending the method of Leigh to magnesium, Reitz and Smith divided the Fermi stiffness into two parts: (1) the full-zone term and (2) the overlap-hole term. They found that the behavior of the filled-zone energy term made pure magnesium unstable with respect to a strain which changes the c/a ratio at constant volume, and that the overlap at the b position in pure magnesium is necessary to balance this instability. In addition, the existence of the p-type overlap is required to give agreement with the observed values of the shear constants c_{44} and C' for pure magnesium. Therefore, according to Reitz and Smith and to Eros and Smith, both b and p types of overlap are present in pure magnesium.

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[18] C. Zener, Acta Cryst. **3**, 346 (1950).

[19] J. R. Reitz and C. S. Smith, Phys. Rev. **104**, 1253 (1956).

[20] J. Trivisonno and C. S. Smith, Acta Met. **9**, 1064 (1961).

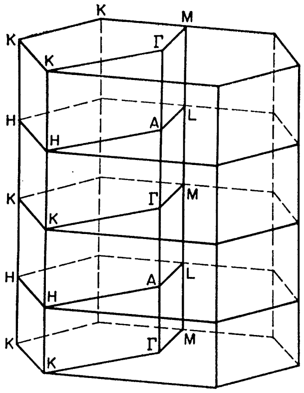

FIG. 3. The double zone in k space chosen to represent the Fermi surface in magnesium.

More recently, however, Falicov[21] calculated the band structure and Fermi surface of magnesium. These calculations resulted in a more accurate description of the BZ structure. According to Falicov, nine electron overlaps of three different kinds exist in the BZ of magnesium. Referring to the double zone in k space, Fig. 3, these overlaps are specified as follows:

(1) One electron overlap around Γ, henceforth referred to as the Γ overlap, with an oblate spheroidal shape. The radii from Γ to the surface, within 20% accuracy, are

$$\left.\begin{aligned} r_{00,1}&=0.058, && \Gamma\to A\\ r_{10,0}&=0.255, && \Gamma\to M\\ r_{11,0}&=0.253, && \Gamma\to K \end{aligned}\right\}\text{third zone.}$$

Here the indices refer to the reciprocal lattice. This overlap is in fact similar to the b overlap of Fig. 2.

(2) Two identical overlaps around K, the K overlap. Each overlap has the shape of a cigar of triangular cross section. The radii from K, within 20% accuracy, are

$$\left.\begin{aligned} r_{00,1}&=0.277, && K\to H\\ r_{11,0}&=0.073, && K\to \Gamma\\ r_{11,0}&=0.044, && K\to M \end{aligned}\right\}\text{third zone.}$$

(3) Six identical overlaps around L, the L overlap. The radii from L are

$$r_{00,1}=0.029,\quad L\to M:\ \text{fourth zone}$$

$$r_{00,1}=0.050,\quad L\to M:\ \text{third zone}$$

$$\left.\begin{aligned} r_{10,0}&=0.022, && L\to A\\ r_{12,0}&=0.043, && L\to H \end{aligned}\right\}\text{third and fourth zones.}$$

The holes in the first and second zones are in a single, multiply connected region around Γ, the Γ hole, which makes contact with the zone near the twelve H points. The hole is described as consisting of:

(1) A hexagonal-shaped ring placed in the plane ΓKM. The radii from Γ are:

10, 0 direction, $\Gamma\to M$: internal radius 0.415
external radius 0.452
11, 0 direction, $\Gamma\to K$: internal radius 0.405
external radius 0.606

with the total height of the ring about 0.125.

(2) Twelve tentacles emanating from the top and bottom of the ring and making contacts with the zone boundaries in very small regions near the H points of the double Brillouin zone. The approximate dimensions of the areas of contact, measured from H, are

$r_{00,1}=0.044$, $H\to K$: first zone
$r_{00,1}=0.044$, $H\to K$: second zone
$r_{11,0}=0.012$, $H\to L$: first and second zones.

Now that the BZ of pure magnesium has been specified, let us proceed to determine how it is affected by lithium alloying, and how this effect is reconciled with the observed values for the shear constants of the alloy. Since the alloy retains the hcp structure characteristic of magnesium, the BZ remains, with some modifications, essentially that of magnesium. Determining the exact nature of these modifications is a rather difficult task and requires a study of the band structure of the alloy. For the purposes of the present discussion, however, let us describe the BZ modification in a simple and perhaps naive manner that is nevertheless consistent with the present measurements of the elastic constants. The effect of lithium alloying may be considered the sum of two effects: (1) removing electrons from the BZ and (2) changing the BZ dimensions through a change of the lattice parameters a and c.

The first of these two effects results, generally speaking, in an increase of the volume of the electron hole and a reduction of the volume of the electron overlap. This may be illustrated by referring, e.g., to the Γ overlap. The Γ overlap in the ΓA direction may be represented schematically as in Fig. 4. Let us say the line NN indicates the volumes of the hole in the second zone and the overlap in the third zone of pure magnesium. Upon alloying with lithium, electrons are removed from the zone and NN is lowered to the new position $N'N'$, where it is seen that the volume of the hole in

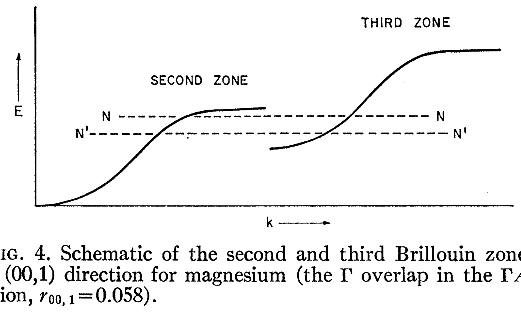

FIG. 4. Schematic of the second and third Brillouin zones in the (00,1) direction for magnesium (the Γ overlap in the ΓA direction, $r_{00,1}=0.058$).

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[21] L. M. Falicov, Phil. Trans. Roy. Soc. (London) **225**, 55 (1962).

the second zone increases and the volume of the overlap in the third zone decreases. If this process were continued, eventually the overlap would disappear completely. In a particular direction, this effect, of course, is felt most strongly upon the smaller overlaps. For example, at a given Li concentration the Γ overlap along the *c*-axis direction ($r_{00,1}=0.058$) would be more affected than the *K* overlap in the same direction ($r_{00,1}=0.277$). In fact, it is easy to visualize that at a certain atomic percent of lithium, the Γ overlap may disappear completely while the *K* overlap is only slightly reduced. Throughout this discussion it has been tacitly assumed that the effect of removing electrons from the BZ is uniform in all directions. In reality this is not the case, of course. Perhaps this is not a bad assumption in the present case, however, since the electron-to-atom ratio for the alloy varies at most by 8% from its value in pure magnesium.

The second effect, that of the change in the BZ dimensions, is brought about through a change of the lattice parameters *c* and *a* with alloying. According to Table V, both constants decrease, thus leading to an increase in the size of the BZ. It is observed however, that the rate of decrease of *c* with percentage of lithium is about four times larger than the rate of decrease of *a*. It follows then that the height of the BZ (its dimension in the *c*-axis direction) increases faster than its lateral dimensions. A close examination of the data in Table V reveals, however, that even in the alloy with 14% Li, the changes in *c* and *a* are very small, and therefore result in a correspondingly small increase in the dimensions of the BZ, 0.327% in the lateral direction and 0.785% in the *c* direction (about twice the lateral change). Increasing the size of the BZ at constant electron-atom ratio essentially makes available more low-energy states for the electrons in each zone. Hence, referring to Fig. 4, it is obvious that this effect brings about a lowering of $N'N'$, particularly for the Γ and *L* overlaps in the *c* direction.

The combined action of the above two effects, then, is to bring about an increase in the volume of the electron hole and a decrease in the volume of the electron overlap, the effect being strongest upon the smaller overlaps in the *c* direction. That is, of the three overlaps, Γ, *K*, and *L*, the *L* overlaps in the *c* direction in the fourth and third zones ($r_{00,1}=0.029$ and $r_{00,1}=0.050$) and the Γ overlap in the third zone ($r_{00,1}=0.058$) are apt to be most affected by alloying. The disappearance of an overlap would bring about a discontinuity in one or all of the shear constants. Since no such behavior is observed in the variation of the shear constants with electron-atom ratio (Fig. 1) we conclude that although some of the overlaps present in pure magnesium may be reduced in size upon alloying with lithium, none seem to vanish completely.

According to Leigh, the Fermi term may be regarded as composed of three parts: contributions from a filled zone, from overlap electrons, and from electron holes. A treatment of the filled zone is a necessary device for obtaining the magnitude of the Fermi contribution; it yields a term which will not change with alloying. There are two effects involved in the contributions from overlap electrons. Under shear, there is a shift of the overlap electron-energy surfaces with the zone faces as the Brillouin zone distorts. There is also a transfer of electrons from those faces receding from the origin to those approaching it. The shift of the energy surfaces with the faces yields a positive term in both the c_{44} and C' shears. However, since the results under discussion are those with constant lattice parameters (i.e., the BZ faces are stationary), this contribution need not be considered here. On the other hand, the transfer phenomenon, which is still allowed in this case, results in a larger negative contribution in both c_{44} and C'. The effect of holes is similar to that of overlapping electrons, except that their contribution from shifting as a whole with the zone faces is negative. Again, for the same reasons mentioned above, this contribution need not be considered. On the other hand, the transfer of holes, under shear, from one face to another is just the same as a transfer of electrons, so this still yields negative terms. Hence it is seen that at constant volume, these transfer phenomena under shear, as well as the increase in the volume of electron hole and the decrease in the volume of the electron overlap upon alloying with lithium, all tend to render the Fermi stiffness more negative, in agreement with Eq. (11b).

The effect of alloying is strongest upon the shear constant $\mathcal{C}$ (Table VIII). This is because only in a shear corresponding to $\mathcal{C}$ are the faces that contain the Γ*A* and *LM* overlaps (these are the overlaps that are most susceptible to changes with alloying) moved relative to the origin of the BZ.

To conclude, the present results on the shear constants of Mg-Li alloys suggest that the BZ of the alloy is essentially that of magnesium with some minor modifications. These modifications, at best, amount to reducing the size of the overlaps and increasing the size of the electron holes. These changes are more pronounced in the *c*-axis direction.

Finally, the expressions for α, *N*, and Z^2 are used to

TABLE VIII. Change in the elastic shear constants of dilute magnesium-lithium alloys per 0.01 decrease in electron-to-atom ratio, expressed in units of 10^{12} dyn cm^{-2}.

	$\mathcal{C}$	C'	c_{44}
Δ(ion-core)[a]	0.00271	0.00033	0.00019
Δ(Coulomb)[a]	−0.01834	−0.00217	−0.00233
Δ(Fermi)[a] = Δ(overlap-hole)	−0.00603	−0.00014	0.00011
Total	−0.02166	−0.00198	−0.00203
Δ(Coulomb)[b]	−0.0181	−0.00210	−0.0011
Δ(overlap-hole)[b]	−0.0201	−0.00334	−0.0039
Total	−0.0382	−0.00551	−0.0050

[a] Present calculations.
[b] Reference 11.

TABLE IX. Comparison of the Fermi stiffness C_{F0} used in this paper with those used by other authors. Units are 10^{12} dyn cm^{-2}.

Experiment	$\mathcal{C}$	C'	c_{44}
Present	-0.261	-0.006	0.005
Ref. 19	0.078	0.033	$\cdots$
Ref. 11	-0.451	-0.023	$\cdots$

compute the change in the overlap-hole term, Coulomb term, and ion-core term per 0.01 decrease in the electron-atom ratio, i.e., $\Delta x = 0.01$, for each of the shear constants $\mathcal{C}$, C', and c_{44}. The resulting values are compared with the corresponding ones obtained by Eros and Smith using the theory of Reitz and Smith (Table VIII). The results of Eros and Smith are approximately twice as large as the present ones. This agreement is rather good in view of the fact that the Fermi stiffness used by Eros and Smith is almost twice as large as the one used in this investigation (Table IX). A further factor that may have contributed to this observed difference is that the values of $(1/C_0)(\Delta C/\Delta x)$ which led us, upon substitution in Eq. (11), to the expressions for α, N, and Z^2 were evaluated at room temperature (Table VI) and not at 0°K as required by their theory.

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Approximate Quantum Numbers for *d*-Band States in Transition Metals*

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A simple procedure for classifying *d*-band states is proposed and applied to the *d* bands of Cu. It is found that most of the spectral structure arises from covalent *d-d* interactions, with *s-d* hybridization playing a minor but significant role.

I. INTRODUCTION

THE electronic structure of transition and noble metals is characterized by the presence of tight-binding *d* bands overlapping broad, nearly-free-electron *s-p* conduction bands. Though the *d* bands are narrow, their width (≈ 4 eV) is still much greater than the strength of the spin-orbit interaction λ. Thus, one says that the orbital angular momentum is quenched, and the *g* factors of magnetic electrons are close to 2.

Because of the complexity of the *d*-band structure, attempts are often made to construct simple models which still retain the essential features of the tight-binding structure. Thus, one often sees models which retain only the crystal-field terms which contribute to the triplet-doublet splitting of the $\Gamma_{25'}$-Γ_{12} levels at $\mathbf{k}=0$ in cubic crystals. One of us has shown,[1] however, that in Cu this term contributes less than 10% of the total splitting at $\mathbf{k}=0$. The remaining 90% actually comes from the covalent two-center overlap integrals which are neglected in the crystal-field model.

The purpose of this paper is to present and analyze a qualitative classification of *d* states which is free of the defects of previous simple models. Our terminology is constructed in analogy with the usual classification of vector waves as longitudinal or transverse. The transverse states may be further divided into right and left circularly polarized. For phonons and magnons it is well known that although this classification is exact only along directions of high symmetry, it remains approximately valid for most values of $\mathbf{k}$ in the Brillouin zone.

This suggests that for a general group of states for which $\mathbf{L}$ would be a good quantum number in the absence of interatomic overlap, we should take the direction of $\mathbf{k}$ itself as an axis of quantization. For acoustic phonons and magnons (which correspond to $L=1$), this immediately generates the longitudinal ($m_k=0$) and transverse ($m_k=\pm 1$) classification.

Another reason for regarding m_k as an approximate quantum number is that it is useful in describing *s-d* interactions when the *d* levels overlap the lowest *s-p* conduction band. One then finds that, although near Brillouin zone edges, Bragg scattering may cause the lowest conduction band to have *p* character, the *p* state in question still corresponds exactly to $m_k=0$ along lines of high symmetry; and that the lowest conduction band is almost purely $m_k=0$ throughout the Brillouin zone. It has been shown[1] that the *s-d* interaction itself is virtually isotropic, so that only the $m_k=0$ *d* band interacts directly with the lowest conduction band. Thus, the $m_k=\pm 1, \pm 2$ *d* bands are virtually unaffected

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[1] F. M. Mueller, Phys. Rev. **153**, 659 (1967).