

TABLE III. Comparison of lifetimes as obtained from Hall and drift measurements on four representative samples.

Sample	Type	Measurement	$\Delta(1000/T)$	$m$	$\tau$ $\mu$ sec	$s$ cm/sec	Drift measurement	
							$\tau$ $\mu$ sec	$s$ cm/sec
W3-3	P	$R=0.0R_p$	$0.0075\pm 0.001$	$0.036\pm 0.005$	$0.48\pm 0.1$		<1	
W7-E	N	$R=0.5R_n$	$0.025\pm 0.003$	$0.44\pm 0.05$		$370\pm 70$		$450\pm 30$
W3-5	P	$R=0.5R_p$	$0.0055\pm 0.001$	$0.10\pm 0.01$	$2.0\pm 0.3$		$\sim 2$	
W12B-4	N	$R=0.5R_n$	$0.020\pm 0.003$	$0.35\pm 0.05$	$35\pm 5$		$32\pm 5$	

## CONCLUSIONS

Current carrier lifetime can be deduced from Hall coefficient and resistivity measurements without recourse to the injection of excess minority carriers or the measurement of short time intervals. For reasonable sizes of samples this method allows the measurement of lifetimes in the  $0.1\mu$ sec range, and will detect changes in lifetime of the order of  $0.01\mu$ sec. On the other end of the range it will measure a  $1000\mu$ sec lifetime to about 10 percent and will just distinguish the difference be-

tween  $\infty$  life and  $10^4\mu$ sec. Its chief advantage lies in the measurement of very short lifetimes.

In using this method the best procedure is to use a  $c$  factor as small as possible, so that any changes in lifetime associated with the intrinsic region will be minimized.

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## Brillouin Zone Investigation of Mg Alloys. I. Hall Effect and Conductivity

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The Brillouin zone structure of hexagonal metal, in particular magnesium as calculated by Jones, has been examined by Hall measurements. The theory predicts a strong dependence on alloying, and the Hall data obtained on alloys of magnesium with aluminum or silver seem to corroborate Jones' theory. In the case of the silver alloys, the absolute value of the Hall constant decreases linearly as a function of alloying addition (0.1 at percent silver decreases the Hall constant by 5 percent). In the aluminum alloys the effect is not so great (0.1 at percent aluminum decreases the Hall constant by  $\sim 2$  percent) and a break in the Hall constant *versus* composition curve is detected. This break can be interpreted as being due to Brillouin zone overlap in the  $c$  direction.

Familiar conductivity rules for alloys are examined in the light of Jones' theory and it is shown that deviations from these rules are to be expected for the alloys of divalent hexagonal metals. A broad experimental program is outlined.

## I. INTRODUCTION

ALTHOUGH the electronic structure of the metals in the first column of the periodic table may be regarded as rather satisfactorily established, this is not the case for the divalent hexagonal metals of the second column. More data on the properties of these metals and their alloys are necessary to develop theories concerning their general behavior.

Figure 1 shows the first Brillouin zone for pure close-packed hexagonal magnesium as deduced by Jones.<sup>1</sup> The density of states as suggested by Mott<sup>2</sup> is given in Fig. 2. The Brillouin zone is bounded by  $\{0002\}$ ,  $\{1100\}$ , and  $\{1101\}$  faces. Since this prism can contain

only 1.743 states/atom, Jones has added the 6 truncated prisms to the  $A$  faces such that 2 states/atom are available. Consequently in pure magnesium, overlap takes place in the  $a$  direction into these prisms but not in the  $c$  direction. The calculations show that there is no energy discontinuity at the edges labeled  $Q$ .

Jones has also shown that small overlap across the boundary surface of a Brillouin zone compresses the zone in the direction perpendicular to the surface concerned, resulting in an expansion in this direction in the real lattice. When silver is added to magnesium, the average electron-atom ratio for the alloy is reduced and there is less overlap in the  $a$  direction relative to pure magnesium. Consequently a contraction in this direction should occur in the real lattice in addition to any contraction due only to the size effect of the ions. This has been found to be the case by actual x-ray

<sup>1</sup>H. Jones, Proc. Roy. Soc. (London) A147, 400 (1934); Physica 15, 13 (1949); Phil. Mag. 41, 663 (1950).

<sup>2</sup>W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (Institute of Metals, London, 1948), Chap. XXVIII.

measurements.<sup>3</sup> Raynor has also found that when indium which has 3 outer electrons is added to pure magnesium, the  $c$  parameter decreases (due to size effect) up to 0.75 atomic percent addition. Beyond 0.75 percent the  $c$  parameter increases. The explanation appears to be that at an electron-to-atom ratio of 2.0075 the truncated prisms have been filled and overlap begins to occur in the  $c$  direction in the Brillouin zone.

## II. HALL EFFECT

The experimental corroboration of the Brillouin zone theory for magnesium so far has come from x-ray data alone. A more direct approach to the study of Brillouin zone overlap can be achieved by examining the effect of alloying on the Hall constant. The effects that should be observed are outlined below and preliminary results on dilute magnesium alloys containing silver and aluminum are presented.

One can write

$$R = - \left| \frac{1}{e} \left\{ \frac{n_1 \mu_1^2 - n_2 \mu_2^2}{(n_1 \mu_1 + n_2 \mu_2)^2} \right\} \right|, \quad (1)$$

where  $R$  is the Hall constant,  $\mu$  is the mobility, and  $n$  is the number of charge carriers per cc, and subscripts 1 and 2 refer to electrons and holes, respectively.

In pure magnesium because of the overlapping Brillouin zone, the configuration of the 3s electrons is such that conduction must be considered a two-zone process. Further, since pure magnesium has a negative Hall constant the process is one in which electron conduction predominates. In such a two-zone system, the effect of changing the relative number of electrons to holes upon the Hall constant will depend on the relative values of their mobilities. Without the latter information, it is impossible to separate the effects due to either electrons or holes.

If magnesium is alloyed with elements of Column I, the effect would be to reduce the size of the Fermi sphere, and should cause a decrease in the number of overlap electrons and an increase in the number of holes. Alloying magnesium with elements of Column III or IV should have an opposite effect. As stated

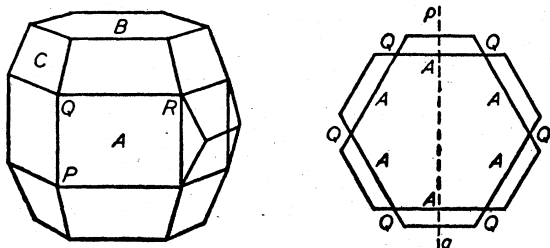


FIG. 1. (a) First Brillouin zone of magnesium as proposed by H. Jones. (b) Equatorial section of (a).

<sup>3</sup> W. Hume-Rothery and G. V. Raynor, Proc. Roy. Soc. (London) A177, 27 (1940); G. V. Raynor, Proc. Roy. Soc. (London) 180, 107 (1942); R. S. Busk, Trans. Am. Inst. Mining Met. Engrs. 188, 1460 (1950).

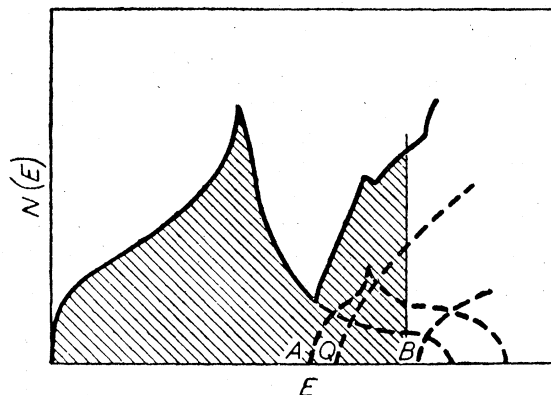


FIG. 2. Density of states for magnesium as proposed by N. F. Mott.

above, the sign of the change of the Hall constant in magnesium resulting from alloying cannot be predicted without prior knowledge of the charge carrier mobilities. However, as elements of Column III or IV are added to magnesium a point will be reached where overlap will take place across the  $B$  faces in the  $c$  direction (see Fig. 1). At this composition, some abrupt change in the Hall constant *versus* composition curve would be expected, since the effect resulting from holes would change abruptly.

Preliminary measurements have been made on pure magnesium and on magnesium alloys containing small amounts of aluminum or silver. They were kindly supplied to us by Professor Dorn of the University of California who had obtained them from the Dow Chemical Company. The measurements were carried out at room temperature using a technique described elsewhere.<sup>4</sup> The results are plotted in Fig. 3. The absolute value of the Hall constant is reduced by additions of either silver or aluminum. The magnitude of the changes (an addition of 0.1 at percent of silver changes the Hall constant by 5 percent) seems to verify the assumption that alloying changes the electronic configuration of magnesium rather radically, although the exact interpretation of the experimental results is not clear. The slope of the Hall constant curve *versus* composition for aluminum is not as steep as that for silver; the ratio of slopes is 2.4 to 1. The curve of the Hall constant for aluminum additions indicates a break between 1.3 and 1.8 at percent aluminum; but the break in the x-ray  $c/a$  curve is at 0.75 at percent as reported by Raynor.<sup>3</sup> Therefore the Hall measurements were repeated. The last point was reproducible to within 1 percent but the point for 1.3 percent aluminum was less reproducible and seemed to be temperature dependent which may be the result of overlap occurring as a result of thermal heating.<sup>5</sup>

<sup>4</sup> Albert I. Schindler and Emerson M. Pugh, Phys. Rev. 89, 295 (1953).

<sup>5</sup> It should be noted that Raynor did not make x-ray measurements between 0.75 and 2 at percent.

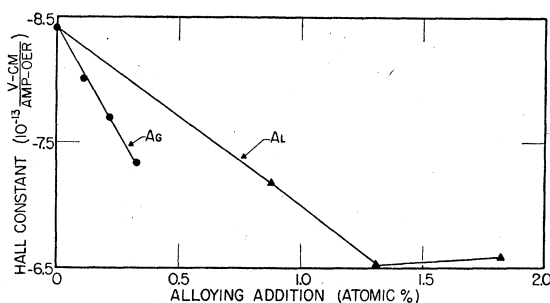


FIG. 3. Hall constant as a function of alloying additions.

In Fig. 4, the number of electrons per atom is calculated assuming a one-zone system (in which only the electrons are conducting). The calculations then show magnesium to have 1.74 electrons per atom. The correct calculations for the number of holes as well as the number of electrons requires a knowledge of their respective mobilities.

### III. CONSIDERATIONS OF CONDUCTIVITY RULES

Speculations may be made concerning the electrical resistivity of dilute magnesium alloys. Linde's rule states that the increase in resistivity of a metal per atomic percent addition of a second metal, aside from an additive constant, is proportional to  $(\Delta Z)^2$ , the square of the difference in valences of the two metals concerned. This rule was based on experiments with monovalent metal solvents. It received theoretical justification by Mott<sup>6</sup> whose theory treated the conduction electrons as though they were free and assumed only non-overlapping solvents. The validity of Linde's rule in the vicinity of Brillouin zone overlap is questionable and should be checked for divalent hexagonal metals.

For a dilute solid solution one usually writes the resistivity  $\rho$  as

$$\rho = m^*/Ne^2(p_i + p_0),$$

where  $m^*$ ,  $N$ , and  $e$  are the effective mass, the number per unit volume, and the charge of the electron, respectively.  $p_i$  is the scattering probability in a pure metal arising from displacement of the atoms from their mean position due to thermal vibration and is therefore temperature dependent.  $p_0$  is the scattering probability arising from perturbation to the periodic field when foreign atoms are introduced and is usually considered temperature independent. Normally the increase in

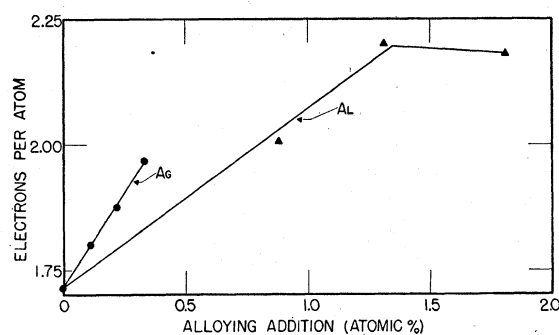


FIG. 4. The number of electrons per atom as a function of alloying additions.

resistivity due to the presence of a second metal is said to be due to  $p_0$  which is proportional to  $(\Delta Z)^2$ .

An implicit assumption exists that the effect of temperature and alloying addition on the resistivity are separable and additive ( $p_0$  is not temperature dependent and  $p_i$  is not dependent upon solute concentration). This may not be valid when the solvent is such that alloying additions change the amount of overlap and consequently the temperature dependence of the overlap. To our knowledge the dependence of scattering probability upon alloying addition as a function of  $c/a$  has not been studied. One would expect.

(1)  $p_i$  to be dependent upon  $c/a$ , and upon Brillouin zone overlap.

(2)  $p_0$  to be temperature dependent near an overlap.

A corollary of Linde's rule is Matthiessen's rule, which states that the increase in resistance of a metal due to a small concentration of another metal in solid solution is independent of the temperature, or that  $\partial\rho/\partial t$  (where  $t$  is temperature) is independent of concentration. By the above arguments  $p_i$  for hexagonal metals depends upon  $c/a$  and upon Brillouin zone overlap. Consequently  $\partial\rho/\partial t$  should depend upon concentration in magnesium alloys.

In view of the results of the Hall measurements and in order to examine the validity of the conductivity rules, a broad experimental program has been outlined and is being undertaken. Hall and conductivity measurements are being made on an extended series of these alloys as a function of temperature. Measurements on single crystals will give the properties as functions of crystal orientation. If a similar program is conducted on alloys of other hexagonal metal, x-ray studies will be necessary to determine how the Jones theory applies when the anisotropy is different from that in magnesium.

<sup>6</sup> N. F. Mott, Proc. Cambridge Phil. Soc. 32, 281 (1936).