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Transport Properties of Dilute Binary Magnesium Alloys

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Unusual lattice parameter behavior in dilute binary magnesium alloys has been observed by Raynor and others, and has been attributed to a Brillouin zone overlap phenomenon suggested by Jones. The primary purpose of this paper is to show that if the overlap model is even only qualitatively correct, measurements of electron transport properties should be sensitive to electron overlap. Such measurements have been made on the resistivity, temperature variation of resistivity, Hall coefficient, and thermoelectric power. Monovalent and divalent additions to magnesium are found to cause the Hall coefficient and thermoelectric power to vary monotonically with composition, but trivalent and quadrivalent additions cause these measurements to go through extrema associated with the zone overlap. It is proposed that both the Hall coefficient and the thermoelectric power may be expressed as the sum of two contributions. One contribution is directly related and therefore is linear to electron concentration. The other contribution arises essentially from everything else, particularly the perturbations upon the ion core potential when a foreign atom is introduced into the lattice. This latter contribution may be obtained directly from measurements on the magnesium-cadmium system. A simple subtraction then provides the electronic contribution for the alloy under question. A band picture is invoked to qualitatively justify this approach. Finally, this paper also demonstrates that Matthiessen's rule and Linde's rule are not valid for dilute magnesium alloys.

I. INTRODUCTION

RAYNOR, in a series of papers,[1] demonstrated that dilute monovalent additions to magnesium cause the crystallographic c/a ratio to decrease with increasing concentration, dilute trivalent or quadrivalent additions after some initial concentration cause it to increase, but dilute additions of divalent cadmium cause no change. Essentially the same results were later reported by Busk.[2] Raynor rationalized this behavior in terms of the Jones overlap theory.[3] This latter theory states that when the Fermi surface overlaps a Brillouin zone face, an interaction occurs between the Fermi surface and the zone face. This interaction may be likened to a longitudinal stress which causes a contraction of the spacing between the zone faces that have been overlapped. In the real lattice, expansion must then occur in the corresponding crystallographic direction. Coupled with the additional effect of the relative ion size of the impurity atom, the Jones model could be used to qualitatively describe how the lattice parameters of magnesium should change with alloying. Recently Goodenough, McClure, Marcus, and Slater[4] indicated that the Jones treatment of the overlap problem is incomplete. For our purposes of discussion, however, it is adequate.

Salkovitz and Schindler[5] have proposed that if overlap occurs, then the behavior of the overlapping electrons should be mainifested in measurements of electron transport properties. Preliminary Hall measurements have already given credence to this proposal.[6] It is the main purpose of the current paper to evaluate in terms of the overlap model extensive measurements of the resistivity, the thermal variation of resistivity, Hall coefficient, and thermoelectric power for a series of dilute magnesium alloys. A secondary goal is to check the validity of Matthiessen's rule and Linde's rule for these alloys.

II. EXPERIMENTAL PROCEDURE

The above measurements were made on pure magnesium and on a series of dilute single-phase binary magnesium alloys.[7] The solutes were monovalent lithium and silver, divalent cadmium, trivalent aluminum, indium and thallium, and quadrivalent tin and lead. The compositions studied are listed in Table I. Specimens were obtained in the form of annealed extruded polycrystalline strips. Each strip was cut into two specimens, one a Hall specimen, the other a resistivity specimen which was also used for the thermoelectric measurements. The Hall specimen was 5 cm ×1 cm ×0.1 cm, with the variation in width and thickness kept to $\pm\frac{1}{2}\%$. The individual resistivity specimens varied in length from 9.54 cm to 29.30 cm, in width from 0.412 cm to 0.640 cm, and in thickness from 0.212 cm to 0.240 cm.

The resistivity data were obtained by using the Reeves modification of the Kelvin double bridge.[8] For

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* Metallurgy Division.

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[1] W. Hume-Rothery and G. V. Raynor, Proc. Roy. Soc. (London) **A177**, 27 (1940); G. V. Raynor, Proc. Roy. Soc. (London) **180**, 107 (1942).

[2] R. S. Busk, Trans. Am. Inst. Mining Met. Engrs. **188**, 1460 (1950).

[3] H. Jones, Proc. Roy. Soc. (London) **A147**, 400 (1934); Physica **15**, 13 (1949); Phil. Mag. **41**, 663 (1950).

[4] J. B. Goodenough, Phys. Rev. **89**, 282 (1953); J. W. McClure, Phys. Rev. **98**, 449 (1955); P. M. Marcus, Phys. Rev. **98**, 1552 (1955) and private communications; J. C. Slater, ASM Theory of Alloy Phases, p. 1 (1956).

[5] E. I. Salkovitz and A. I. Schindler, Phys. Rev. **91**, 234 (1953).

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

[7] Some of these samples were very kindly furnished by Professor J. Dorn, University of California; the rest were obtained directly from the Dow Chemical Company.

[8] F. A. Laws, *Electrical Measurements* (McGraw-Hill Book Company, Inc., New York, 1938), second edition.

TABLE I. Compilation of data as measured.

Specimen No.	Alloying agent	Atomic percent	Resistivity ρ_{20} ($10^{-6}\Omega$ cm)	$d\rho/dt$($10^{-8}\Omega$ cm/°C)	Hall coefficient $\left(10^{-13}\frac{\text{v cm}}{\text{amp-oe}}\right)$	Thermoelectric power[a]	
						$S_{300°\text{K}}$	$S_{78°\text{K}}$
1	Pure Mg		4.450	1.656	−8.42	−0.223	−0.142
2	Ag	0.11	4.586	1.638	−8.01	+0.015	+0.434
3		0.22	4.626	1.674	−7.70	+0.148	+0.781
4		0.33	4.711	1.656	−7.34	+0.268	+1.09
406		0.495	4.865	1.652		+0.575	+1.18
407		0.528	5.007	1.646	−6.76	+0.795	+1.51
408		0.998			−6.06	+1.036	+1.70
409		1.953	5.947	1.600		+1.79	+2.26
422	Li	0.49	4.875	1.613	−6.83	+0.395	+0.376
156		2.55	6.377	1.651	−1.73	+1.834	+1.377
117		4.42	7.668	1.674	+1.13	+2.78	+1.918
118		7.63				+4.21	+2.112
119		10.4				+5.47	+2.900
120		13.9				+7.97	
396	Cd	0.55	4.883	1.644	−7.08	+0.375	+1.02
397		1.01	5.141	1.620		+0.630	+1.26
398		1.92	5.734	1.645	−4.87	+1.12	+1.87
399		3.92			−2.90	+1.82	+2.16
725		8.64	9.664	1.539	+0.72	+3.03	+2.78
724		12.68			+3.19	+3.88	+3.23
400	Al	0.29	5.032	1.605	−7.87	−0.102	+0.138
401		0.53	5.583	1.606		−0.112	+0.261
402		0.80	6.091	1.594	−7.07	−0.143	+0.335
8		0.88	6.218	1.608	−7.18		
9		1.31	7.036	1.610	−6.53		
403		1.64	7.688	1.530	−6.60	−0.255	+0.550
10		1.82	8.081	1.586	−6.58		
404		2.18	8.646	1.509	−6.67	−0.397	+0.660
405		2.41	9.064	1.494	−6.69	−0.462	+0.630
391	In	0.446	5.198	1.543	−7.31	+0.039	+0.757
392		0.862	6.422	1.599	−6.85	+0.062	+0.950
393		1.46	7.617	1.491	−6.19	+0.067	+0.979
394		2.30	9.180	1.490	−5.96	−0.057	+1.21
395		3.01	10.287	1.429		−0.158	+1.27
16		3.74	11.971	1.447	−6.97	−0.421	+1.20
14		6.76			−9.84	−1.40	+0.566
15		10.57			−14.56	−2.78	+0.290
13	Tl	1.32	8.772	1.614	−3.62	+0.393	
12		2.94	13.469	1.480	−1.73	+0.647	
11		4.84			−2.71	+0.739	
380	Sn	0.047	4.786	1.632	−8.37	−0.174	+0.81
5		0.10	5.062	1.697	−8.71	−0.370	+0.183
381		0.17	5.452	1.598	−8.26	−0.382	+0.240
6		0.19	5.523	1.678	−8.13	−0.499	+0.221
7		0.29	6.001	1.612	−7.49	−0.618	+0.429
382		0.54	7.200	1.592	−8.43	−0.909	+0.446
383		1.08	9.606	1.509	−8.65	−1.365	+0.511
384		2.04	11.646	1.493	−8.65	−1.625	+0.555
65	Pb	0.24	5.782	1.599	−7.98	−0.366	+0.336
66		0.37	6.467	1.593	−7.66	−0.502	+0.444
388		1.32	11.276	1.404	−7.32	−1.091	+0.79
389		2.01			−7.24	−1.377	+0.79

[a] The convention used above was to consider the thermoelectric power positive relative to the magnesium circuit if the hot junction was negative. In plotting the various graphs, however, the data have been normalized to specimen No. 1, the pure magnesium sample (99.98% Mg).

the measurements the specimens were placed in a hermetically sealed box and were heated by radiation from long heater strips placed within the box, below and parallel to the specimens. The temperature of the specimens could be raised slowly at a controlled rate from room temperature to 10° or 15°C above, permitting measurements of the temperature variation of resistivity.

The thermoelectric power data were obtained in the following manner. Against each end of the specimen a pure magnesium wire was clamped, forming a thermocouple, so that the thermoelectric emf for a given alloy

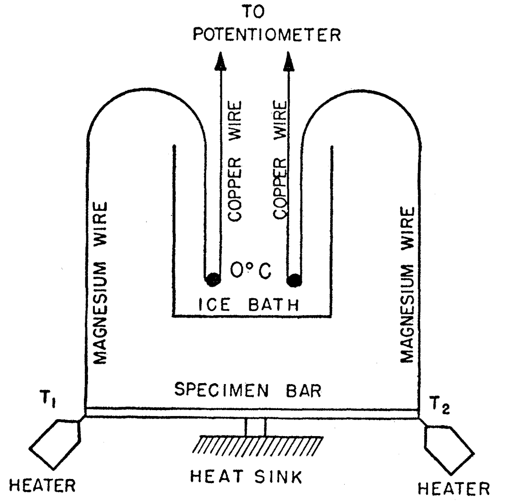

FIG. 1. Arrangement for thermoelectric power experiments.

was measured relative to the wire. The remaining ends of each of the magnesium wires were connected mechanically to copper wires and thence to a potentiometer. (See Fig. 1.) The junctions between copper and magnesium were kept at a constant temperature by a suitable cold bath. Incorporated into the clamps which forced the magnesium wire against the specimen at each end, were small controllable electric heater elements as well as chromel-alumel temperature measuring junctions. The latter were superimposed on the contact points made by the magnesium wire with the specimen. A clamp at the center of the specimen conducted heat to a massive iron stand supporting the apparatus. This heat sink left one-half of the specimen length at room temperature, the temperature gradient existing only between the heated end and the clamped center of the bar.

Two sets of measurements were made in all instances. First the left end of the specimen was kept at room temperature, and the right end heated, then the left end was heated while the right end was kept at room temperature. The emf for each set of measurements was plotted against temperature. The thermoelectric power for the particular sample was taken to be the average of the slopes of the two plots. During the course of the work it was discovered that the magnesium wire used for comparison was less pure than the "pure magnesium" used as a specimen and as base metal for all the alloys. Consequently, a net thermoelectric power was found between the magnesium wire and the pure magnesium sample. This reading was subtracted from all subsequent readings so that in the graphs which follow it is the thermoelectric power relative to the pure magnesium sample which is plotted.

To obtain the relative thermoelectric power of the various alloys with the cold junction at liquid nitrogen temperature, a modification of the room temperature technique was used. The same pure magnesium reference wires were clamped to each end of the specimen together with a chromel-alumel thermocouple for temperature measurement. This assembly was then suspended in liquid nitrogen. One end of the specimen projected a short distance from the bath allowing the junction temperature to rise above that of the liquid nitrogen. By changing this exposed length in small increments, a plot of emf *versus* junction temperature-difference was obtained and the slope of this graph yielded the relative thermoelectric power with respect to the magnesium wire. Again, to evaluate any non-uniformity of the specimens and reference wire in these tests, data were taken for each end of the specimen used alternately as the cold junction, and for interchanged positions of the reference wires.

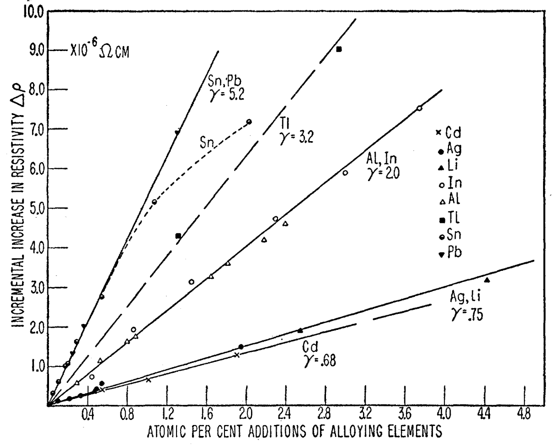

FIG. 2. Increase in resistivity of magnesium due to alloying.

Hall measurements were made only at room temperature by means of a technique already described elsewhere. The reader is referred to the earlier paper[6] for more details.

III. RESULTS

(a) Resistivity of Alloys

The room temperature resistivity measurements have already been reported[9] so that only brief mention will be made here. Linde's rule, which holds quite well for alloys of monovalent elements, states that

$$\Delta\rho/A = k_1 + k_2(\Delta Z)^2, \qquad (1)$$

where $\Delta\rho/A$ is the increase in resistivity per atomic percent addition of solute, ΔZ is the difference in valence between the solute and solvent atoms, and k_1 and k_2 are constants depending on the period (of the periodic table) to which the solute belongs.

For the magnesium alloys indicated, Fig. 2 shows the incremental increase in resistivity, $\Delta\rho$, over that of pure magnesium, plotted against alloying content. Except for the tin additions, the data fall on good

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[9] E. I. Salkovitz and A. I. Schindler, Phys. Rev. 98, 543 (1955).

straight lines, suggesting a linear increase of $\Delta\rho$ with composition. Further, the curves fall into groups. For the monovalent additions silver and lithium, the slope $\gamma=0.75$; for the trivalent additions aluminum and indium, $\gamma=2.0$; and for the quadrivalent additions of lead and at least the initial additions of tin, $\gamma=5.2$. It is evident then that although γ and therefore $\Delta\rho/A$ depend on the valence of the solute atom, these parameters do not depend on the period to which the solute atoms belong, nor upon ΔZ^2. Consequently for these alloys Linde's rule is not valid.

(b) Matthiessen's Rule

Nordheim has shown that the resistivity ρ, for an alloy may be expressed thus,

$$\rho=\rho_T+\rho_i, \tag{2}$$

where ρ_T is the thermal contribution to the resistivity due to lattice vibrations, i.e., phonon scattering, and is therefore temperature-dependent, and ρ_i is the contribution due to impurities which is temperature-independent. Hence for dilute alloys of a given metal the temperature variation of the resistivity $d\rho/dT$ must be a constant, independent of concentration of the solute. This is known as Matthiessen's rule.

Figure 3 is a typical plot of resistance against temperature for the specimens studied. In this case it is for sample 7 containing 0.29 atomic percent tin. From the slope of the curve, a value of 1.61×10^{-8} ohm cm/°C is obtained for $d\rho/dT$. Superimposed on this graph is a line with a slope corresponding to a $d\rho/dT$ of 1.49×10^{-8} ohm cm/°C which would be that for sample 384 containing 2.04 atomic percent tin. Clearly the small amount of scatter in the data cannot account for the two different slopes, and it may be concluded that $d\rho/dT$ is not the same for these two materials. In fact, increasing the tin content by only 1.7% changes $d\rho/dT$ by about 8%.

A very sensitive test for the validity of Matthiessen's rule is the plot, as in Fig. 4, of a dimensionless quantity, the ratio $(d\rho/dT)_A/(d\rho/dT)_{\text{Mg}}$ *versus* a second dimensionless quantity, the ratio $(e/a)_A/(e/a)_{\text{Mg}}$, where e/a represents the electron concentration obtained using the usual Hume-Rothery valences. The subscript A refers to the alloy investigated, while the subscript Mg refers to the pure magnesium sample. When some of these data were first reported, it appeared, on a compressed plot, that $d\rho/dT$ had a relatively constant value before overlap and another after. This is not the case. Indeed the quantity $d\rho/dT$ decreases rapidly with electron concentration, so that Matthiessen's rule is not valid for these magnesium alloys at room temperature.

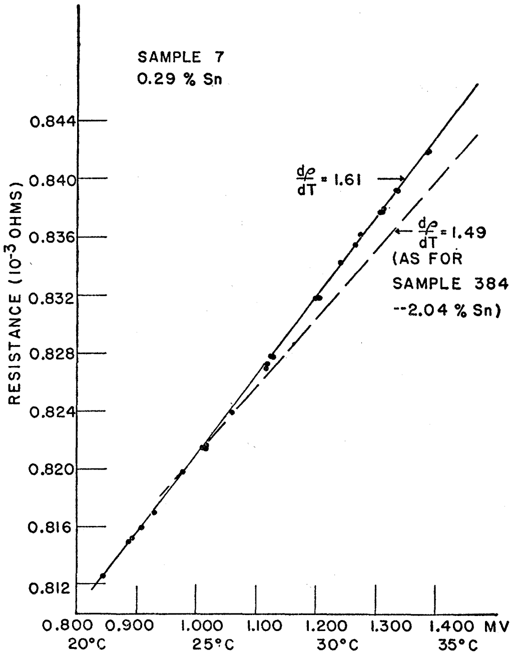

FIG. 3. Resistance of a magnesium-tin alloy as a function of temperature.

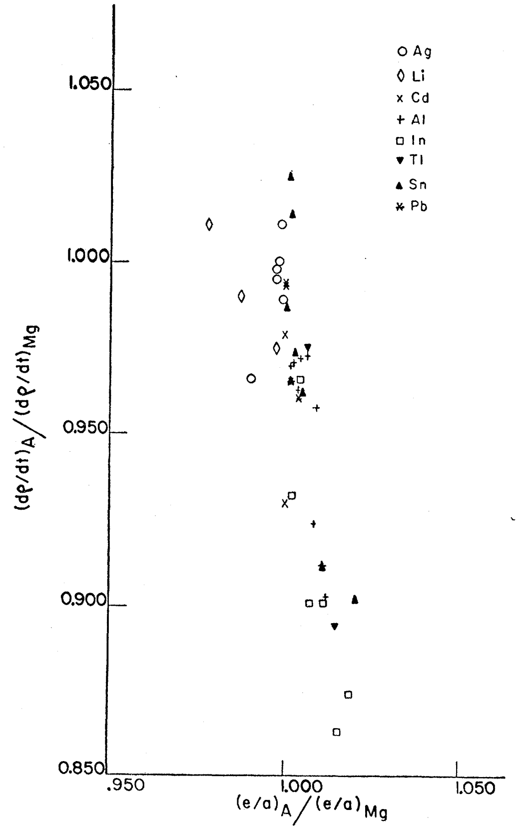

FIG. 4. Ratio of $d\rho/dT$ of magnesium alloys relative to $d\rho/dT$ for pure magnesium *versus* ratio of electron concentration of magnesium alloys relative to electron concentration of pure magnesium.

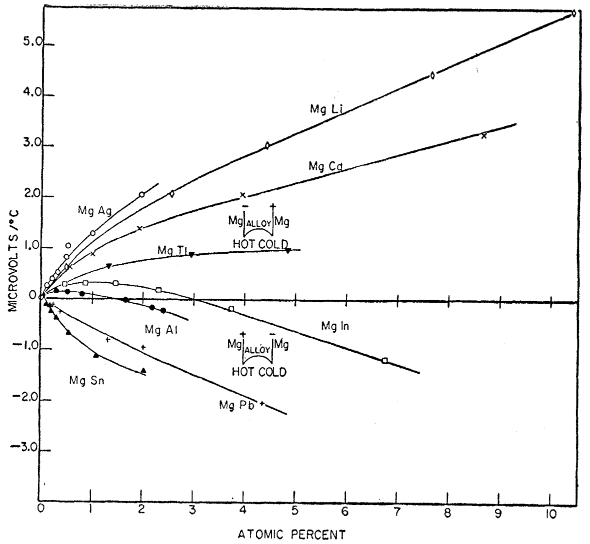

FIG. 5. Thermoelectric power ($S_{300^\circ K}$) at room temperature of various dilute magnesium alloys relative to pure magnesium *versus* composition.

(c) Thermoelectric Power

Figure 5 is a composite plot of $S_{300^\circ K}$, the thermoelectric power at room temperature of the various alloys measured relative to pure magnesium, *versus* composition. The pertinent features to note are the following: (a) $S_{300^\circ K}$ increases monotonically with increasing composition for additions of monovalent silver and lithium, and divalent cadmium. (b) Although cadmium when added to magnesium does not change the electron concentration, it nevertheless produces a sizable change in the thermoelectric power. (c) Trivalent indium and aluminum generate a different type of relationship between $S_{300^\circ K}$ and composition: in these two cases, the thermoelectric power goes through a maximum. For thallium however, only three points are available so that it cannot be established whether or not its curve would go through a maximum. (d) Quadrivalent tin shows a maximum at very low concentration. (Unfortunately magnesium-lead alloys of this concentration were not available.)

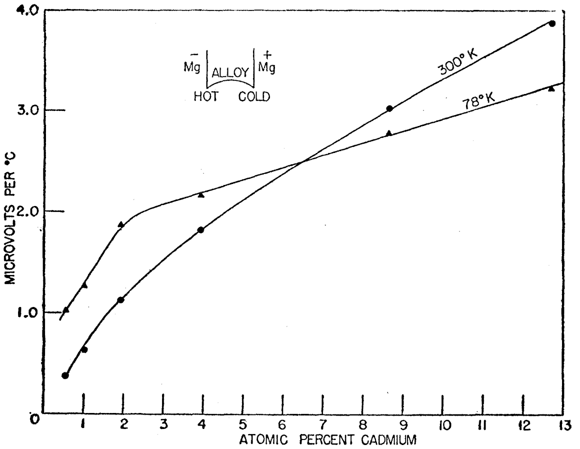

FIG. 7. Thermoelectric power at 78°K and 300°K for magnesium-cadmium alloys as a function of alloying.

Thermoelectric power data at 78°K and 300°K as a function of percent composition are plotted in Figs. 6, 7, and 8 for silver, cadmium, and lead additions. For additions of silver and lead, the thermoelectric power relative to magnesium is higher at 78°K than at 300°K; this is also true for cadmium additions up to at least 4%. The reversal in sign between the magnesium-lead data at 300°K and 78°K should be noted. For comparative purposes at 78°K the effect of additions from the fifth period have been plotted in Fig. 9. Again, a valence effect is quite apparent. And again at 78°K, cadmium, although not changing the electron concentration of magnesium, nevertheless has a considerable influence on its thermoelectric power.

Data for the magnesium-aluminum alloys at 78°K, 195°K, and 300°K are represented in Fig. 10. The

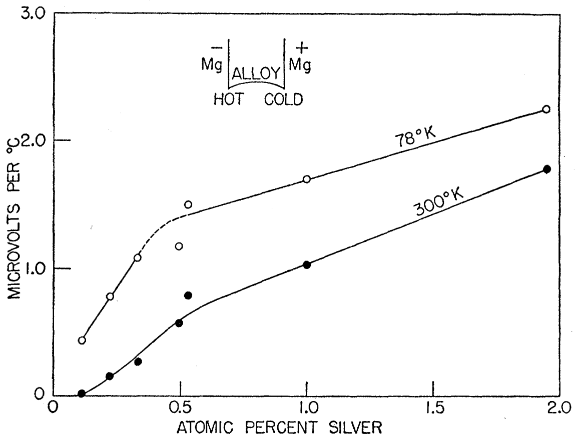

FIG. 6. Thermoelectric power at 78°K and 300°K for magnesium-silver alloys as a function of alloying.

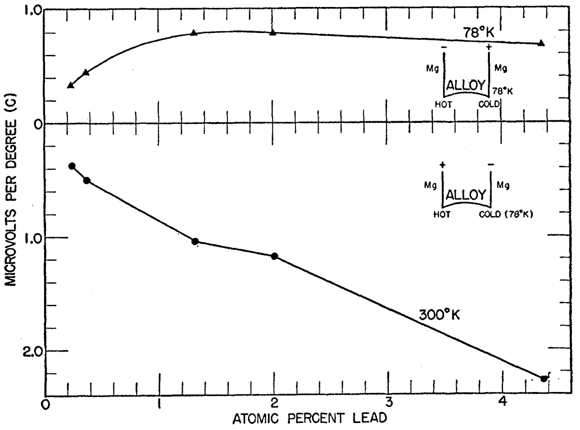

FIG. 8. Thermoelectric power at 78°K and 300°K for magnesium-lead alloys as a function of alloying.

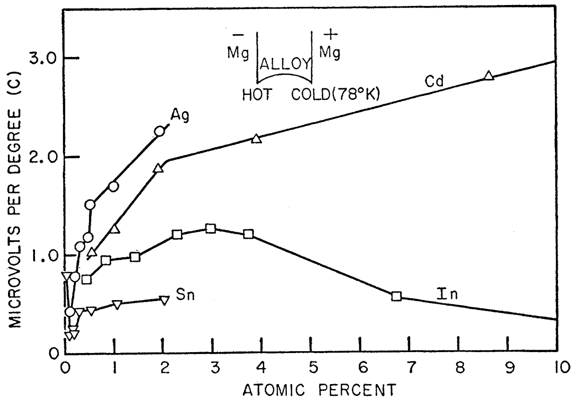

FIG. 9. Thermoelectric power at 78°K for magnesium alloyed with fifth period elements, silver, cadmium, indium, or tin, as a function of alloying.

compositions at which the maxima occur may be observed to increase with decreasing temperature. This is clearly illustrated in Fig. 11, where these maxima have been plotted against temperature for indium as well as aluminum additions. To a first approximation, a linear relation between maxima and temperature is obtained in this temperature range.

(d) Hall Coefficient

Figure 12(a) is a plot of the room temperature Hall coefficient *R versus* alloying addition, while Fig. 12(b) is a magnified portion of the latter. The pertinent features, here, resemble those for the room temperature thermoelectric power curves, namely: (a) additions of silver, lithium, or cadmium cause the absolute value of the Hall coefficient to decrease regularly; (b) again, cadmium has a large effect; (c) the Hall coefficient goes through a minimum for additions of indium or aluminum; (d) with additions of tin, *R* goes through a maximum at the lowest concentration, and then through a minimum. For lead additions, since only four compositions were studied, it can only be stated that *R* appears to decrease rapidly initially and then level off.

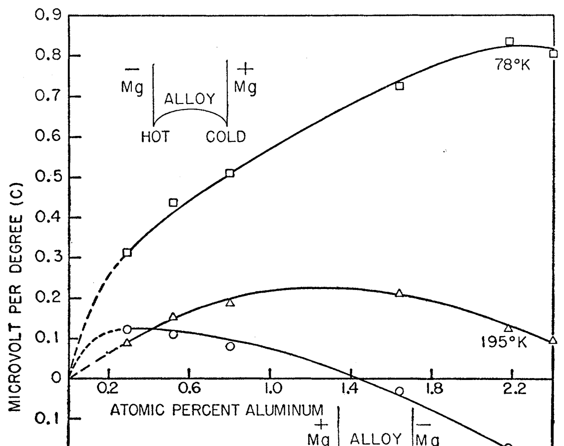

FIG. 10. Thermoelectric power of magnesium aluminum alloys at 78°K, 195°K, and 300°K as a function of alloying.

IV. DISCUSSION

So far no consideration has been given to the relative sizes of the various solute atoms. In Fig. 13 is a portion of the periodic table listing the atomic sizes of these solutes relative to magnesium. The data are for the free ion, not for the ion in solid solution which, though more appropriate, are not available.

In Fig. 2 the slopes, γ, of the various curves represent the incremental increases in resistivity relative to pure magnesium per atomic percent addition of solute. It is apparent that γ_{Ag} is approximately equal to γ_{Li}, yet the ion sizes of silver and lithium are quite different. The same comparison may be made for γ_{Al} and γ_{In}. We must conclude that the predominant factor in determining γ is the valence of the solute. (We cannot account for the value of γ_{Tl}.) By comparison, the relative ion size is not nearly as significant within the range of ion sizes considered. In turn, Fig. 4, which shows $d\rho/dT$ varying rapidly with electron concentration, implies that the dominant factor in the temperature variation of these alloys at room temperature is again the electron concentration. We must conclude that the Nordheim separation itself, and therefore Matthiessen's rule, is not valid at room temperature for these alloys.

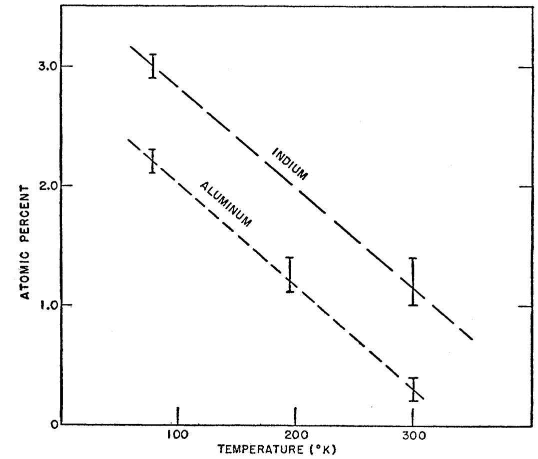

FIG. 11. Compositions at which maxima occur in the thermoelectric power for magnesium-aluminum and magnesium-indium alloys as a function of temperature.

As indicated, the relative valence of solute atom to solvent atom has a predominant effect on the resistivity and the other transport properties; however, since cadmium is divalent just as magnesium, the large effects on these properties must be explained in terms of some other parameters. One such parameter is the perturbation on the ion core potential due to alloying. We suggest that the nature of this perturbation may be deduced from the transport properties of magnesium-cadmium alloys.

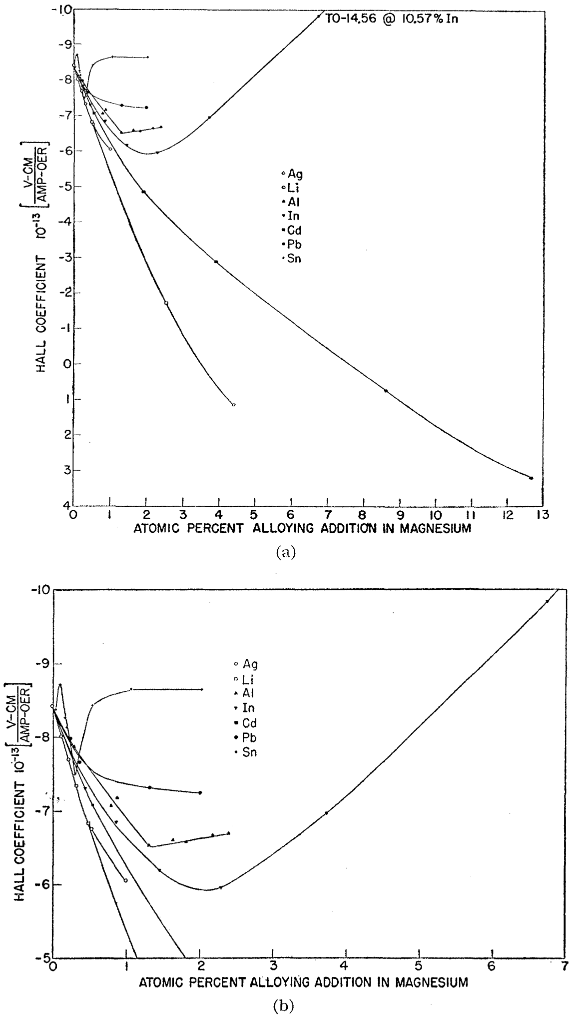

FIG. 12. (a) Hall coefficients of magnesium alloys as a function of alloying. (b) Magnified portion of Fig. 12(a).

	I	II	III	IV
1	1 H			
2	3Li -2.2%	4Be	5 B	6 C
3	11Na	12Mg	13 Al -10.3%	14 Si
4	19K	20Ca	21Sc	22Ti
	29 Cu	30Zn	31 Ga	32Ge
5	37Rb	38Sr	39Y	40Zr
	47Ag -9.8%	48Cd -5%	49 In -1.7%	50Sn -1%
6	55Cs	56Ba	57La	72Hf
	79Au	80Hg	81 Tl +7.2%	82 Pb +9.1%

FIG. 13. Portion of periodic table showing atomic diameters relative to magnesium.

Consider the difference $S-S_{\text{Cd}}=S_e$, where S is the measured thermoelectric power for an alloy of given composition, and S_{Cd} is the value for a magnesium-cadmium alloy of the same composition. We suggest, then, that S_e represents the electronic effect of alloying arising from a change in the filling of the energy bands as the electron concentration is varied, and that the subtraction of S_{Cd} has corrected approximately for other effects on the thermoelectric power (due to the impurity) such as the perturbations on the ion core potential. The plots of S_e *versus* atomic percent addition (Fig. 14) are curves with initial slopes which are greater for quadrivalent additions (tin, lead), somewhat less for trivalent additions (aluminum, indium, thallium) and least for monovalent additions (lithium and silver). However, in all cases S_e decreases linearly with increase of electron concentration. (Note that the electron concentration decreases for monovalent additions.) The described behavior would be consistent with a density of states curve, $g(\epsilon)$, which decreases with energy ϵ at the Fermi level of pure magnesium and has a finite negative curvature there. (See the recent discussion by Jones[10] on the sign of the thermoelectric power.) An increase of electron concentration as produced by trivalent and quadrivalent additions would make the slope $g'(\epsilon)$ more negative, and in first

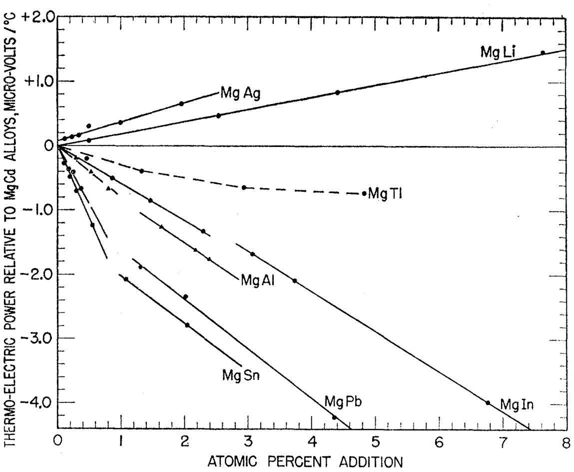

FIG. 14. Thermoelectric power relative to magnesium-cadmium (S_e) plotted against composition.

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[10] H. Jones, Proc. Phys. Soc. (London) **68**, 1191 (1955).

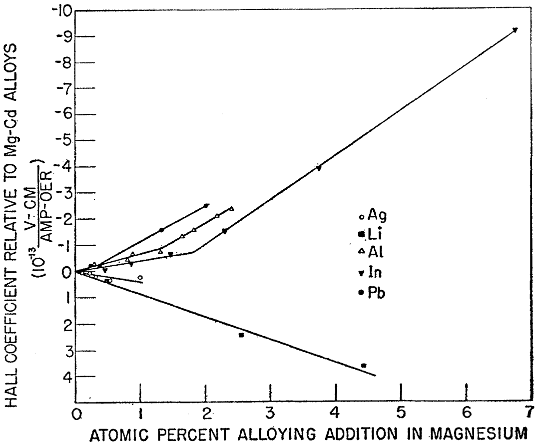

FIG. 15. Hall coefficient relative to magnesium-cadmium (R_e) plotted against composition.

approximation the changes in S_e would be linear in energy, hence linear in electron concentration, precisely as indicated in Fig. 14.[11]

In the case of magnesium-tin and magnesium-lead, the curves for S_e *versus* atomic percent addition show an abrupt algebraic increase in slope near 1 atomic percent, and for magnesium-aluminum and magnesium-indium lesser breaks between 2 and 3 atomic percent additions. These breaks could be associated with the appearance of a zone overlap in accordance with other evidence of breaks in physical properties near these concentrations. Thus the occurrence of overlap should suddenly increase $g'(\epsilon)$, since additional states are being added beyond the overlap point, and the Jones formula[10] would then show an algebraic increase in S_e.

If we interpret the variation of S_e as arising from electronic effects, namely changes in $g(\epsilon)$ and $g'(\epsilon)$, then the additional part of the change in S produced by alloying, which we have roughly considered equal to S_{Cd}, consists of a smoothly rising contribution (with atomic percent composition).[12] The combination of these two parts produces a maximum in S for the magnesium-indium and magnesium-aluminum cases as noted above. It is interesting that this maximum persists at lower temperatures but shifts to higher concentration and, in fact, the concentration of the maximum seems linear in temperature.

The initial curvature of the plots of S, the measured thermoelectric power, *versus* composition have not been discussed. The method of analysis employed above (e.g., subtracting S_{Cd} from S to get S_e) eliminates a major portion of the curvature, and yields approximately straight lines for S_e. However in a paper in preparation, we treat the initial curvature of S in terms of the Friedel theory.[13]

It is also possible to assume that the measured Hall coefficient, R, may be resolved into a portion R_e arising from the conduction electrons, and a portion depending upon all the other effects. As before, this latter portion may be obtained from the Hall coefficient data for the magnesium-cadmium alloy. That is, $R_e = R - R_{\text{Cd}}$. In Fig. 15, R_e has been plotted against atomic percent composition for the various alloys. Again straight lines are obtained for magnesium-silver and magnesium-lithium and straight lines with abrupt breaks are obtained for magnesium-aluminum, magnesium-indium, and magnesium-lead. The compositions at which the breaks occur in the S_e and R_e plots, appear in Table II. The small differences between the two types of measurements might be resolved if more samples in the critical region of composition were available. The explanation of how the slope of the R_e curves are related to the valence of the solute atom must be similar to the argument put forth in the case of S_e.

As for the thermoelectric power, the formulation of a two-band model for the Hall coefficient leaves much to be desired, for it leads to ambiguous predictions concerning the effect of alloying except for the interesting case of the magnesium-cadmium system indicated below.

From band theory, an expression for the Hall coefficient is obtained as follows:

$$R = \frac{2}{eN_xN_y}\int\left\{\left(\frac{\partial E}{\partial k_y}\right)^2\frac{\partial^2 E}{\partial k_x^2} - \frac{\partial E}{\partial k_y}\frac{\partial E}{\partial k_x}\frac{\partial^2 E}{\partial k_x \partial k_y}\right\}\frac{dS}{|\text{grad}E|}, \tag{3}$$

where

$$N_x = 2\int\left(\frac{\partial E}{\partial k_x}\right)^2\frac{dS}{|\text{grad}E|}, \tag{4}$$

and the integration is over the surface of the Fermi distribution.

The sign and magnitude of $\partial E/\partial k$ and $\partial^2 E/\partial k^2$, etc., are particularly sensitive to the conditions of overlap; therefore sensitivity of the Hall coefficient to overlap should be expected. Details of this sensitivity, however, depend upon details of the slope and curvature of the Fermi surface. The necessary detailed calculations of the Fermi surface for pure magnesium have not been made, even in the recent work by Trlifaj.[14]

TABLE II. Compositions at which breaks occur.

Alloying agent	Thermoelectric power $S_{300°\text{K}}$	Hall coefficient
Al	1.3 at. %	1.3 at. %
In	2.3–3 at. %	1.8 at. %
Pb	0.8 at. %	0.4 at. %
Sn	0.8 at. %	...

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[11] The positive intercept for the Mg—Ag curve may be due to a trace impurity present in this alloy series.

[12] Consistent with this picture, we find that the effect on the thermoelectric power due to cold work (a lattice effect) is independent of electron concentration. This work will be reported in detail in a later publication.

[13] J. Friedel, J. phys. radium 14, 561 (1953).

[14] M. Trlifaj, Czech. J. Phys. 1, 110 (1952).

Equation (4) may be expressed in terms of the number of charge carriers, n, and their mobilities μ, thus:

$$R=-\frac{1}{ec}\left\{\frac{n_1\mu_1^2-n_2\mu_2^2}{(n_1\mu_1+n_2\mu_2)^2}\right\}, \tag{5}$$

where the subscripts 1 refer to electrons, and the subscripts 2 refer to holes. It is well to recall that in the derivation of Eq. (4) the relaxation time is assumed to be constant over the Fermi surface, and that the temperature is above the Debye temperature which is about room temperature for magnesium. In going to Eq. (5), it is further assumed that the relaxation times for the two bands are independent and that the metal is isotropic.

Recognizing that these assumptions have been made, one is nevertheless inclined to believe that Eq. (5) must approximate the correct expression for the Hall coefficient. As alloying takes place, the electron and hole mobilities will be altered; particularly so, in the neighborhood of overlap. But sufficient information is not available to predict how R should vary with alloying. In addition, when foreign atoms are introduced into the lattice, in this case the magnesium lattice, there should be expected a perturbation upon the density of states curve, upon the magnitude of the energy gaps, and upon the interaction between the Fermi surface and the Brillouin zone. It is for this reason that the electron transport measurements of the magnesium-cadmium alloys are important. Since the electron concentration of the magnesium cadmium alloys may be taken as constant independent of concentration, these measurements should be very sensitive to the above perturbations. By making the subtractions described earlier in this section, it is possible to see how the "electronic" or "impurity" contribution of R and S vary with composition for a given alloy system. It is this contribution which is found to be valence-sensitive.

In pure magnesium the number of overlapped electrons is equal to the number of holes in the first zone. When dilute additions of cadmium are made, the equality between electrons and holes is not upset. Therefore the mobilities of the electrons and holes must be affected. For the magnesium-cadmium alloy system, then, the Hall coefficient and the conductivity may be represented by

$$R=-\frac{1}{nec}\left[\frac{\mu_1-\mu_2}{\mu_1+\mu_2}\right], \tag{6}$$

$$\sigma=ne[\mu_1+\mu_2] \tag{7}$$

$$-R\sigma=\frac{1}{c}[\mu_1-\mu_2]. \tag{8}$$

Taking the data from Table I, a plot may be made of the difference in mobilities as a function of composition for the magnesium-cadmium series. This is shown in Fig. 16. Since the Hall coefficient of pure magnesium is negative, electron conduction predominates. As cadmium is added, the hole contribution begins to increase. In the neighborhood of 8% cadmium, the two contributions are equal and the Hall coefficient is zero. At higher compositions, hole conduction predominates; e.g., the magnitude of the hole mobilities becomes larger than that for electron mobilities, and the Hall coefficient becomes positive. It is interesting that the difference in hole and electron mobilities is never very large.

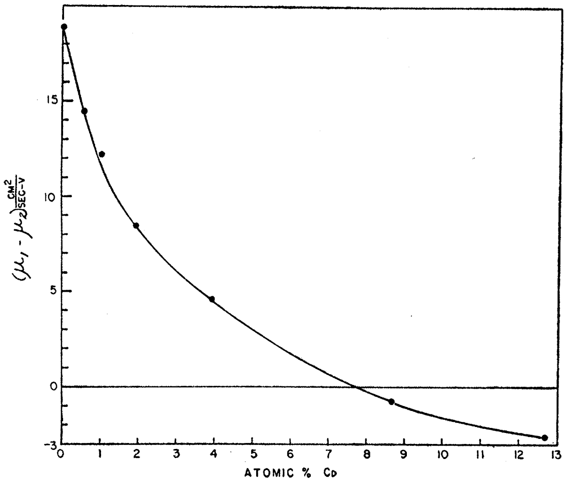

FIG. 16. $(\mu_1-\mu_2)$ for magnesium-cadmium alloys as a function of cadmium content.

CONCLUSIONS

It has been demonstrated that measurements of electron transport properties of dilute magnesium alloys are sensitive to the Brillouin zone overlap phenomena earlier deduced by x-ray techniques. By direct measurement Matthiessen's rule and Linde's rule have been found to be invalid. Thus, contrary to Matthiessen's rule, $d\rho/dT$ varies markedly with composition. The resistivity itself varies linearly with composition, except for the case of the magnesium-tin alloys at higher concentrations. The alloying effect upon the resistivity depends primarily upon the valence of the solute atom and not its size.

Both the thermoelectric power and Hall coefficient go through extrema at compositions approximating the overlap compositions indicated by the x-ray work. It has been demonstrated that the thermoelectric power as well as the Hall coefficient for a given dilute magnesium alloy may be expressed as the sum of two contributions. One contribution, S_e, arises from the direct effect of the electron concentration and is linear with electron concentration; the other contribution arises from all other effects, notably the perturbations upon the ion core potential and may be obtained from the magnesium-cadmium data. The slopes of the curves of S_e *versus* composition may be related to $g(\epsilon)$ and $g'(\epsilon)$. Discontinuities in the slopes of these curves are found in the neighborhood of the zone overlap compositions.

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Thermal Fluctuations in Conductors*

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In this paper we investigate the behavior of a conductor in thermal equilibrium with the surrounding radiation field. We obtain an expression connecting the spectrum of the current fluctuations with the absorption. For small frequencies this reduces to Nyquist's relation. For large frequencies, however, the relation is quite different; namely, the current fluctuations are *proportional* to the (skin) resistance and depend also on the shape of the conductor.

I

THE usual derivations of the Nyquist formula, describing the thermal fluctuations of currents in a conductor, are of three kinds. The first kind uses as the model an electric network; the second kind uses a detailed kinetic model for the conductor; the third kind uses no model at all.[1]

If we use the network model we introduce a large number of tacit and explicit assumptions whose validity is difficult to assess. The complications inherent in any detailed kinetic calculation are only too well known; consequently one uses a simplified model, which enables one to show, at best, that this simplified model is compatible with the relations we expect. We side-step these difficulties if we use a general theory of fluctuations; however, if we want to apply it to a special class of fluctuations, i.e., currents in a metal, we are faced again with the problem of evaluating the very general expressions in terms of the quantities which appear in our problem.

For this reason, in this paper we make use of a fourth approach. We agree that Maxwell's equations with the proper constitutive relations describe correctly the interaction of the electromagnetic field with matter, and worry about the kinetic problem only insofar as this is necessary to specify the constitutive equations and evaluate the material constants. (This is the reason why we do not have to introduce quantum mechanics explicitly; the quantum mechanics is shifted into the constitutive part.)

In other words, we shall couple the conductor to the radiation field surrounding it, and not to a transmission line as in the usual derivation. In this way we can avoid the commonly made specifying assumptions which restrict the results to conductors with frequency-independent resistance, zero self-capacitance, and zero self-inductance.

Our problem then is simply this: What conditions are imposed by Maxwell's equations on the fluctuating currents in a piece of metal if the latter is in thermal equilibrium with the radiation field?

In equilibrium the average flux absorbed by the metal must be equal to the average emitted flux. Since the emitted flux is created by the fluctuating currents in the metal, this gives a relation between the *absorption* and the fluctuating currents. Hence it seems that the absorption is the natural variable to use and we may expect that our result will be simpler if we express the fluctuations in terms of the absorption instead of in terms of the resistance.

[The question was once raised,[2] how far if at all, is the resistance the essential and physical cause of the fluctuation. We see now the answer. The resistance is the cause of the fluctuations as far as the absorption depends on the resistance. As we shall see the functional dependence between absorption and resistance can vary with the physical conditions.]

As our result we will obtain a fluctuation formula

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[1] Network model: H. Nyquist, Phys. Rev. **32**, 110 (1928); M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945). Kinetic model: e.g., C. J. Bakker and G. Heller, Physica **6**, 262 (1939). General fluctuation theory: H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951). For an excellent summary, see J. L. Lawson and G. E. Uhlenbeck, *Threshold Signals* (McGraw-Hill Book Company, Inc., New York, 1950), Massachusetts Institute of Technology Radiation Laboratory Series, Vol. 24, Chap. 4.

[2] E. B. Moullin, *Spontaneous Fluctuations of Voltage* (Clarendon Press, Oxford, 1938).