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Influence of Lattice Scattering on Mathiessen's Rule in Dilute Binary Magnesium Alloys*

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Measurements and analysis of resistivity as a function of temperature are presented for dilute magnesium alloys with solutes Al, Ag, Li, and Cd over the temperature range 4.2–372°K. It is found that previously observed negative deviations from Mathiessen's rule occurring in these alloys can be accounted for by considering the change in Grüneisen θ on alloying and, in fact, a reduced resistivity ρ/ρ_θ is found to have the same dependence on reduced temperature T/θ as pure Mg for all of the nontransition metal alloys studied. Based on the above observation, an empirical method is presented for analyzing the temperature-resistivity characteristic of magnesium alloys containing transition-metal-induced low-temperature resistivity anomalies. This spin term in the resistivity is found to occur at much higher temperatures than previously thought and above the temperature of magnetic ordering varies logarithmically with temperature. The magnitude of the anomaly is found to vary linearly with transition-metal concentration. Both of these findings are in agreement with recent theoretical studies.

I. INTRODUCTION

It is customary to consider the electrical resistivity of a metal as the sum of two terms—one due to thermal vibrations (ρ_i), and the other due to impurities (ρ_0). Mathiessen[1] showed experimentally that ρ_0 depends on the solute concentration and is largely independent of temperature, while ρ_i is temperature-dependent and independent of solute concentration. This leads directly to the usual analytic statement of Mathiessen's rule, which is

$$\left.\frac{\partial\rho(T)}{\partial T}\right|_{\text{alloy}}=\left.\frac{\partial\rho(T)}{\partial T}\right|_{\text{pure solvent}}.$$

The constancy of ρ_0 is always assumed and any departure of $\rho_i(T)$ in alloys from its value in the pure metal solvent is treated as a deviation from Mathiessen's rule.

In early experiments, Linde[2] reported only small positive deviations from Mathiessen's rule for the noble metals containing nontransition element solutes.[3] The polyvalent metals, aluminum and tin, have been studied by Robinson and Dorn[4] and by Alley and Serin,[5] where positive deviations from Mathiessen's rule were found for nontransition element solutes. Salkovitz *et al.*[6] were the first to report negative deviations from Mathiessen's rule in alloys of magnesium containing nontransition metal impurities and measured in the temperature range (20–35°C). Deviations from Mathiessen's rule have been discussed from a theoretical point of view[7] by numerous authors. All conclusions seem to point to the fact that positive deviations would be expected; however, Jones has pointed out that a change in the phonon scattering due to alloying could possibly produce a negative deviation from Mathiessen's rule.

Salkovitz *et al.*[6] found it possible to explain their observation of negative deviations from Mathiessen's rule for dilute binary magnesium alloys by using the Jones overlap model. However, recent determinations[8] of the Fermi surface of magnesium would indicate that all of the suggested Fermi surface overlaps at the zone boundaries have already taken place in the pure solvent. This leads to the speculation that the observed negative deviations from Mathiessen's rule could be explained by considering solely the influence of impurities on the lattice component of resistivity. Such a study required precise determinations of the resistivity over a more extended temperature range than previously reported in binary alloys of magnesium.[6] We wish to report these resistivity measurements made from 4.2 to 373°K on various binary magnesium alloys, and to analyze the results to obtain the concentration dependence of the Grüneisen θ value.

We then go on to show that a plot of the reduced thermal component of the electrical resistivity, ρ/ρ_θ as a function of T/θ, is the same for all of the alloys containing nontransition metal impurities. Using this information, it is possible to separate the anomalous resistivity term in alloys containing transition metal

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[1] A. Mathiessen and C. Vogt, Pogg. Ann. **122**, 79 (1864).

[2] A. Linde, Ann. Physik **15**, 219 (1932).

[3] For discussion and review see F. Blatt, Solid State Phys. 4, 199 (1957).

[4] A. T. Robinson and J. E. Dorin, J. Metals Trans. **3**, 457 (1951).

[5] P. Alley and B. Serin, Phys. Rev. **116**, 334 (1959).

[6] E. I. Salkovitz, A. I. Schindler, and E. W. Kammer, Phys. Rev. **98**, 543 (1955); **105**, 887 (1953); **107**, 1549 (1957).

[7] For discussion and review see H. Jones, in *Handbüch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XIX.

[8] See (a) W. L. Gordon, A. S. Joseph, and T. G. Ech, *The Fermi Surface* (John Wiley & Sons, Inc., New York, 1960). (b) R. W. Stark, T. G. Eck, W. L. Gordon, and F. Moazed, Phys. Rev. Letters **8**, 360 (1960). (c) M. G. Priestly, L. M. Falicov, and Y. Weisz, Phys. Rev. **131**, 617 (1963).

TABLE I. Nominal composition, resistivity, and average values of θ and $r(0)$ for the alloys studied. Identification numbers for the binary nontransition solute magnesium alloys are the same as those used in Ref. 6.

Specimen number	Solute	Nominal conc. at.%	Resistivity (273) $\mu\Omega$-cm	$\frac{10^4}{\rho_p(273)}\left(\frac{d\rho_a}{dT}-\frac{d\rho_p}{dT}\right)$ Ref. 6 (°K^{-1})	$10^4\frac{d}{dT}\left[\frac{\Delta(T)}{\rho_p(273)}\right]$	$\bar{\theta}$ (°K)	$\langle r(0)\rangle_{\text{av}}$
728	Pure Mg		4.052			340	···
406	Ag	0.49	4.382				
409	Ag	1.95	5.479	-1.3 ± 0.2	-1.0 ± 0.2	312	···
117	Li	4.42	6.676	$+0.4\pm0.2$	$+0.2\pm0.2$	319	···
725	Cd	8.64	9.285	-2.6 ± 0.2	-3.2 ± 0.2	264	···
400	Al	0.29	4.545	-1.1 ± 0.2	-0.9 ± 0.2	328	···
402	Al	0.80	5.624	-1.4 ± 0.2	-1.3 ± 0.2	314	···
405	Al	2.41	8.333	-3.9 ± 0.2	-3.6 ± 0.2	300	···
500	Mn	0.056	4.40			325	0.058
501	Mn	0.089	4.51			318	0.087
502	Mn	0.19	4.87			320	0.157
503	Mn	0.4	5.88			295	0.284
504	Mn	0.8	7.03			290	0.452

impurities,[9] making appropriate allowance for the high-temperature deviations from Mathiessen's rule. This separation results in a spin-dependent resistivity component having a concentration and temperature dependence in agreement with the recent theoretical predictions of Kondo.[10]

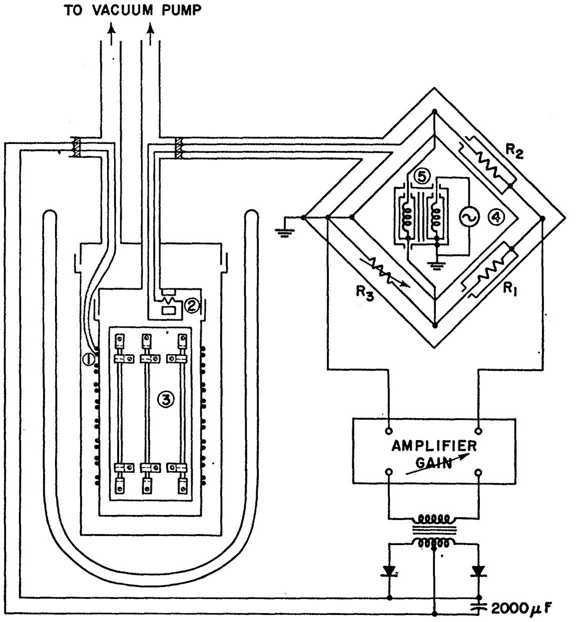

FIG. 1. Resistivity cryostat and temperature control system. The shielding of the bridge is shown in detail including the transformer (5) which isolates the 200 cps generator (4) from the bridge. It should be noted that the bridge balance condition will be frequency and capacity-independent provided $C_1/C_2=R_2/R_1$, where C_1 and C_2 are the shielding capacitances shunted across R_1 and R_2, respectively.

II. EXPERIMENTAL PROCEDURE

The magnesium alloys studied are fully described in the work of Salkovitz *et al.*, and the specimens used in the present work were kindly supplied by these authors. To obtain resistance samples, pieces were cut from the supplied ingots, rolled into 0.01-in. strips, etched, cut into specimens $\frac{1}{8}\times4$ in. long and annealed in a helium atmosphere at 7 cm of Hg at 450°C for 12 h. Table I shows the concentration, resistivity and original identification number of the specimens.[11]

The double chamber cryostat and its temperature controller are shown in Fig. 1. The inner chamber, containing the resistance samples, is filled with a few millimeters of helium exchange gas, and the outer chamber is pumped hard after obtaining measurements at the boiling point of the refrigerant. The temperature is controlled by driving the bifilarly wound heater (1) from the amplified output of a Wheatstone bridge having the resistance thermometer (2) as one of its elements. By adjusting the value of R_3, the temperature in the inner chamber can be maintained between 4.2 and 78°K when liquid helium is the refrigerant, and between 78 and 273°K when liquid nitrogen is the refrigerant. (Care must be taken that overshoot does not occur otherwise the feedback becomes positive.) The gain and stability of the temperature control system are sufficient

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[9] The observation of so-called low-temperature resistance "minima and maxima" in magnesium and identification with transition metal impurities has been discussed by F. T. Hedgcock, W. B. Muir, and E. Wallingford, Can. J. Phys. 38, 376 (1960).

[10] J. Kondo, Progr. Theoret. Phys. (Kyoto) (to be published).

[11] Since the specimens were cut from the ends of the supplied ingots, it was anticipated that inhomogeneities in the ingot might lead to a specimen resistivity different from the value quoted by Salkovitz *et al.* for the ingot. In order to obtain a more reliable value for the resistivity of the specimens, a graph of $[1/\rho(273)][\partial\rho/\partial T]_{273}$ as a function of $1/\rho(273)$ was plotted for each alloy system using the data given by Salkovitz *et al.* The value of the resistance ratio $r(T)\equiv R(T)/R(273)$ was then plotted as a function of temperature and the value of $(\partial r(T)/\partial T)_{273}$, determined. Since

$$\left.\frac{\partial r(T)}{\partial T}\right|_{273}=\frac{1}{R(273)}\left.\frac{\partial R(T)}{\partial T}\right|_{273}=\frac{1}{273}\left.\frac{\partial\rho(T)}{\partial T}\right|_{273}.$$

The resistivity of the specimens was determined from the graph and is listed in Table I.

TABLE II. Resistance ratio as a function of temperature for the binary nontransition solute magnesium alloys listed in Table I.

		$r(T)$			$r(T)$			$r(T)$			$r(T)$
T°K	406	117	728	T°K	725	409	T°K	400	402	T°K	405
4.27	0.0773	0.373_3	0.00246_7	4.24	0.537_4	0.259_5	4.24	0.1242	0.289_3	4.28	0.544_8
6.34	0.0774	0.373_7	0.00246_7	6.34	0.537_4	0.259_2	12.47	0.124_5	0.290_3	7.72	0.544_8
14.15	0.0782	0.373_3	0.00297_5	10.79	0.538_0	0.259_5	15.24	0.1248	0.290_6	10.61	0.544_1
20.10	0.0798	0.374_2	0.00401_0	14.05	0.538_0	0.259_8	18.38	0.1256	0.291_3	12.37	0.544_1
24.76	0.0817	0.376_0	0.00544_2	20.35	0.540_5	0.261_3	20.38	0.1260	0.291_4	15.30	0.544_1
34.8_6	0.0905	0.381_3	0.01250	24.9_2	0.542_4	0.263_8	23.3_0	0.1272	0.292_8	18.71	0.544_8
41.32	0.0999	0.388_0	0.02107	35.0_7	0.550_0	0.272_2	27.1_5	0.1294	0.294_5	20.74	0.545_4
59.39	0.1410	0.417_3	0.0634_3	41.6_5	0.556_5	0.280_7	33.0_1	0.1341	0.299_1	23.4_5	0.546_0
79.9	0.2036	0.461_2	0.1307	59.8_8	0.583_0	0.317_3	42.0_7	0.1457	0.309_3	27.3_8	0.547_2
89.3	0.2467	0.491_2	0.1776	77.9	0.616_3	0.367_3	57.9_5	0.179_8	0.338_2	33.3_6	0.550_3
107.4	0.322_1	0.543_5	0.259_9	90.2	0.641_5	0.405_9	77.9	0.242_6	0.389_8	42.5_8	0.557_2
124.3	0.394_6	0.591_6	0.338_3	108.9	0.682_2	0.468_2	95.3	0.307_0	0.442_8	53.0_1	0.569_4
146.5	0.448_1	0.654_2	0.440_7	125.9	0.717_4	0.525_0	110.8	0.368_9	0.493_1	72.3_9	0.601_1
177.1	0.614_6	0.741_9	0.577_9	147.2	0.761_5	0.597_4	127.8	0.437_9	0.549_6	77.8	0.611_1
198.3	0.703	0.800	0.674_2	179.3	0.825	0.703_1	151.3	0.531_7	0.620_0	92.8	0.641_4
230.5	0.833	0.888	0.817	204.0	0.872	0.783_0	186.8	0.668_8	0.733_5	110.8	0.679_8
273.1	1.000	1.000	1.000	273.1	1.000	1.000	215.5	0.782_6	0.822	129.7	0.717_1
292.2	1.073	1.045	1.078	297.8	1.041	1.074	273.1	1.000	1.000	153.7	0.767_5
309.6	1.137	1.088	1.149	312.2	1.065	1.115	295.9	1.083	1.064	191.4	0.843
329.8	1.213	1.140	1.233	335.0	1.103	1.182	316.1	1.153	1.121	220.0	0.898
351.0	1.292	1.196	1.321	353.3	1.134	1.234	320.4	1.171	1.135	273.1	1.000
371.2	1.370	1.244	1.405	373.6	1.165	1.291	331.8	1.208	1.167	298.2	1.044
							352.2	1.285	1.225	314.8	1.074
							372.7	1.358	1.287	334.0	1.109
										355.2	1.149
										372.7	1.179

to insure constancy of temperature to 0.1% or better for periods of at least 15 min throughout the entire temperature range. Temperatures above 273°K were obtained by immersing the cryostat, with the outer shield removed, in a well stirred water bath.

The temperature of the specimens was measured with thermometers located on the rear of the contact board (3). All temperatures above 20°K were measured using a platinum resistance thermometer. Temperature values were obtained from the published values of the relative thermal component of the resistivity as a function of temperature.[12] Between 4.2 and 20°K, the temperature was measured using a carbon resistance thermometer which was calibrated[13] *in situ*. Three known calibration temperatures were obtained by observing the superconducting transition temperature of lead, tin, and rhenium specimens in the cryostat.

A current potential method with knife-edge pressed contacts was used to measure the resistance of the specimens. The voltages were measured using a galvanometer amplifier having series inverse feedback to increase the input resistance and stability.[14] The specimen current was adjusted manually and kept constant within 0.01% during any set of measurements. Provision was made to reverse the current so that the effect of stray thermals in the potential leads could be reduced. The estimated accuracy of the resistance ratio measurements is 0.2%.

The cryostat described above was designed so that three specimens could be run simultaneously. In practice, measurements were made on two alloys and pure Mg, thus enabling the resistance ratio of the alloys and pure Mg to be compared at a given temperature without recourse to interpolation. Since the accuracy of presentation is limited when the results are presented graphically, the temperature dependence of the resistivity is shown in tabular form. Table II shows the data for alloys containing nontransition metal solutes, whereas Table III shows the data for alloys containing transition metal solutes. We will postpone discussion of the alloys exhibiting resistance anomalies until Sec. III.2. For alloys containing nontransition metal solutes deviations from Mathiessen's rule $\Delta(T)$ can be expressed as the difference between the ideal resistivity of the alloy $\rho_{ia}(T)$ and the ideal resistivity of the pure metal $\rho_{ip}(T)$. Since the total resistivity $\rho(T)$ is given by

$$\rho(T)=\rho_0+\rho_i(T),$$

then

$$\Delta T=[\rho_a(T)-\rho_{0a}]-[\rho_p(T)-\rho_{0p}]. \qquad (1)$$

Experimentally, it is more convenient to measure the resistance ratio $R(T)/R_{273}\equiv r(T)$. Assuming thermal expansion can be neglected, Eq. (1) can be written as

$$\Delta(T)/\rho_p^{(273)}+\rho_{0a}-\rho_{0p}/\rho_p^{(273)} =r_a(T)(\rho_{a(273)}/\rho_p^{(273)})-r_p(T). \qquad (2)$$

We know that $\Delta(T)$ will be zero at $T=0$ and in practice will be zero for $T=4$°K. Thus, the right-hand side of

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[12] G. K. White, *Experimental Techniques in Low-Temperature Physics* (Oxford University Press, Inc., New York, 1959), p. 115.

[13] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[14] D. K. C. MacDonald, J. Sci. Instr. **24**, 232 (1947). See also W. B. Muir, Rev. Sci. Instr. **35**, 408 (1964).

TABLE III. Resistance ratio as a function of temperature for the binary transition solute magnesium alloys listed in Table I. These data are from the thesis of E. Wallingford, University of Ottawa, 1961, and we gratefully acknowledge his permission to quote these results.

500		501		502		503		504	
T°K	$r(T)$	T°K	$r(T)$	T°K	$r(T)$	T°K	$r(T)$	T°K	$r(T)$
1.95	0.08387	1.94	0.1219	1.88	0.2102	4.65	0.354	4.60	0.537
2.66	0.08162	2.96	0.1186	2.96	0.2094	6.80	0.351	6.22	0.539
2.96	0.08069	3.84	0.1162	3.43	0.2082	8.92	0.346	7.62	0.540
3.43	0.08064	4.20	0.1156	3.84	0.2072	13.85	0.338	10.7	0.537
3.84	0.07860	5.37	0.1130	4.20	0.2063	21.7	0.328	19.8	0.525
4.20	0.07796	6.49	0.1108	5.40	0.2034	32.1	0.325	28.8	0.511
5.59	0.07555	7.27	0.1094	6.50	0.2002	36.1	0.327	34.6	0.513
7.20	0.07320	13.0	0.1041	7.35	0.1981	40.2	0.329	38.4	0.514
11.2	0.07093	27.4	0.1043	14.2	0.1873	43.3	0.332	42.0	0.515
25.4	0.07071	33.7	0.1079	30.3	0.1843	46.4	0.335	45.5	0.516
32.8	0.07540	37.9	0.1130	34.7	0.2025	49.3	0.339	48.0	0.518
37.0	0.08035	41.9	0.1183	38.8	0.1910	51.7	0.343	50.9	0.520
41.2	0.08566	48.3	0.1291	45.2	0.1992	54.3	0.347	53.2	0.522
47.8	0.09687	55.0	0.1438	53.4	0.2139	56.1	0.350	55.5	0.524
52.4	0.1075	62.5	0.1635	62.7	0.2337	59.1	0.355	58.1	0.527
57.9	0.1212	77.0	0.2116	69.7	0.2551	68.1	0.381	64.3	0.537
64.6	0.1410	89.4	0.2595	77.0	0.2780	81.9	0.420	75.1	0.556
69.7	0.1575	93.6	0.2756	87.5	0.3159	96.6	0.466	89.4	0.585
81.9	0.2040	100.4	0.3033	96.7	0.3474	109.7	0.508	103.7	0.617
91.6	0.2409	111.8	0.3531	105.1	0.3796	133.5	0.576	125.5	0.665
104.1	0.2974	124.6	0.4082	112.5	0.4094	156.0	0.647	151.0	0.722
111.4	0.3248	133.5	0.4443	125.5	0.4600	183.0	0.733	178.5	0.787
123.9	0.3804	142.5	0.4839	134.5	0.4933	198.0	0.778	195.0	0.824
132.5	0.4162	151.4	0.521	143.0	0.529	273.1	1.000	273.1	1.000
141.6	0.4580	161.3	0.562	152.0	0.564				
150.5	0.4976	168.3	0.592	162.0	0.600				
160.4	0.540	178.4	0.634	168.0	0.627				
167.9	0.571	189.2	0.679	180.0	0.665				
177.7	0.613	197.6	0.712	190.2	0.706				
188.4	0.660	208.0	0.755	209.0	0.775				
197.0	0.695	273.1	1.000	273.1	1.000				
206.8	0.738								
273.1	1.000								

Eq. (2) gives $(\rho_{0a}-\rho_{0p})/\rho_p^{(273)}$ at temperature below 4°K. Hence, the relative deviations from Mathiessen's rule can be obtained by plotting $r_a(T)\rho_{a(273)}/\rho_{p(273)}-r_p(T)$ as a function of temperature. Figure 2(a) shows the results of doing this for the most concentrated alloy from each group using data taken from Tables I and II. Since

$$\frac{(\partial\rho/\partial T)|_a-(\partial\rho/\partial T)|_p}{\rho_{p(273)}}=\frac{d}{dT}\left[\frac{\Delta(T)}{\rho_{p(273)}}\right],$$

the high-temperature slopes in Fig. 2(a) can be compared with the values of $(\partial\rho/\partial T)|_{\text{alloy}}-(\partial\rho/\partial T)|_{\text{pure}}$ quoted by Salkovitz *et al.* These quantities are listed in Table I, and good agreement is found for the various alloys.

The results in Fig. 2(a) show graphically the surprising feature of negative deviations from Mathiessen's rule.

III. ANALYSIS OF RESULTS

1. Alloys Containing Nontransition Metal Impurities

The Grüneisen formula for the resistance of a metal can be written

$$\rho_i(T)/\rho_i(\theta)=1.056(T/\theta)\mathcal{G}(\theta/T),$$

where $\mathcal{G}(\theta/T)$ has been tabulated by Grüneisen and $\rho_i(\theta)$ is the ideal resistivity of the metal at temperature θ. Kelly and MacDonald[15] show how a value of θ may be deduced from resistivity data provided the value of θ is assumed independent of T. They write

$$\frac{d\rho_i(T)/dT}{\rho_i(T)/T}=\frac{d\rho(T)/dT}{(\rho(T)-\rho_0)/T}=\frac{d\gamma(T)/dT}{(\gamma(T)-\gamma_0)/T}$$

$$=1+\left|\frac{x}{G(x)}\frac{dG(x)}{dx}\right|, \tag{3}$$

where $x=\theta/T$. The function on the right-hand side of Eq. (3) has been evaluated as a function of x so that by evaluating the left-hand side of Eq. (3) for a particular alloy, a value of θ can be found at a given temperature. Figure 3 shows θ as a function of temperature for the most concentrated alloys measured. The value of θ remains constant over a 100°K temperature interval with large deviations occurring at both the high and low-temperature limits,[16] and therefore, the average value of the characteristic temperature $\bar{\theta}$ in this temper-

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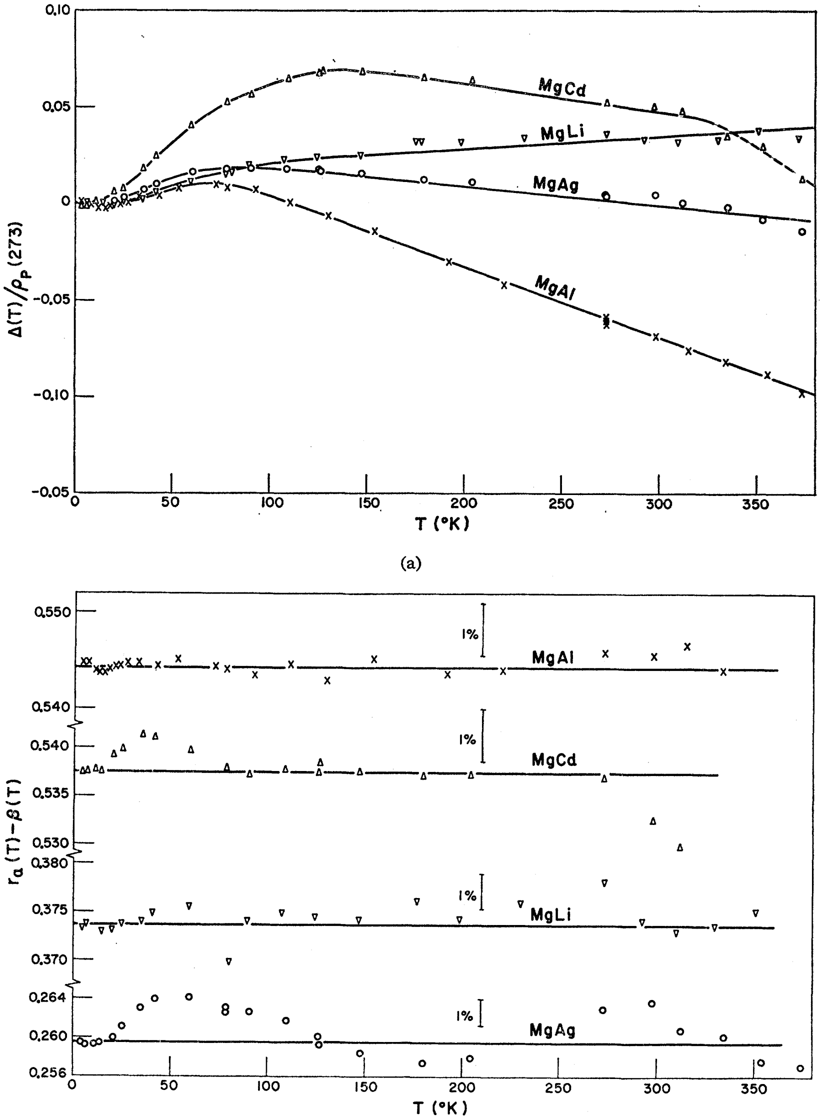
[15] F. M. Kelly and D. K. C. MacDonald, Can. J. Phys. **31**, 147 (1953).

[16] The fit appears to be good in the region expected, i.e., $\frac{1}{5}\theta-\frac{1}{2}\theta$.



(a)

(b)

FIG. 2(a). Deviations from Mathiessen's rule for the binary magnesium, nontransition solute, alloys where $\Delta(T)$ is defined by Eq. (1) in Sec. II. (b) Deviations from Mathiessen's rule expressed in terms of the resistance ratio for the same binary magnesium alloys shown in Fig. 2(a) after proper allowance has been made for a change in the ideal thermal component of the resistivity by altering θ. $\beta(T)$ and $r_a(T)$ are defined in Eq. (5), Sec. III.

ature range can be used to characterize the change in the phonon spectrum due to alloying. Included in Table I are average values of θ for the alloys measured.

If the observed deviations from Mathiessen's rule are due to changes in θ on alloying, then $\rho_i(T)/\rho_i(\bar{\theta})$ plotted as a function of $T/\bar{\theta}$ should yield a curve which is independent of solute and solute concentration as is shown in Fig. 4. A more accurate presentation of the results in Fig. 4 can be achieved by noting that

$$\rho_{ia}(T)/\rho_{ia}(\bar{\theta}_a)-\rho_{ip}(T')/\rho_{ip}(\bar{\theta}_p)=0\,, \qquad (4)$$

when $T'/\bar{\theta}_p=T/\theta_a$. Equation (4) can be expressed in terms of the experimentally more convenient resistance ratio as

$$r_a(T)-\beta(T)=r_a(0)\,, \qquad (5)$$

where

$$\beta(T)=[r_a(\bar{\theta}_a)-r_a(0)]\frac{r_p[(\bar{\theta}_p/\bar{\theta}_a)T]-r_p(0)}{r_p(\bar{\theta}_p)-r_p(0)}\,.$$

Figure 2(b) shows a plot of $r_a(T)-\beta(T)$ as a function of temperature for the alloys measured. There appears to be no significant trend away from the value $r_a(0)$ for any alloy thus indicating that the deviations from Mathiessen's rule observed in these alloys can be satisfactorily accounted for by a change in $\bar{\theta}$ on alloying and that the reduced thermal component of the resistivity, plotted as a function of reduced temperature, is independent of solute and solute concentration for binary nontransition metal alloys having magnesium as solvent.

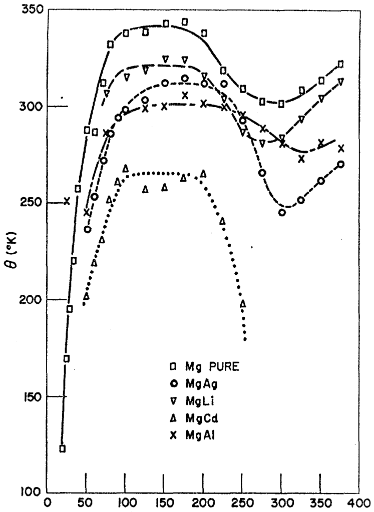


FIG. 3. The Grüneisen θ as a function of T for the most concentrated alloys from the binary nontransition solute group listed in Table I.

2. Results for Alloys Containing Transition Metal Impurities

We assume that what we will now call "normal deviations from Mathiessen's rule" in alloys containing transition metal solutes are identical with those alloys formed with nontransition solutes, and can be accounted for solely by a change in the Grüneisen θ value. Thus, we propose that if θ can be determined for the paramagnetic alloy from the high-temperature resistivity, we should be able to estimate $\rho_i(T)$ for a given θ since

$$\rho_i(T)=\rho_i(\theta)f(T/\theta),$$

where $f(T/\theta)$ is determined from the empirical curve of Fig. 4. In terms of the resistance ratio, this means

$$\begin{aligned} r_i(T) &\equiv r(T)-r(0) \\ &=[r(\theta)-r(0)]f(T/\theta). \end{aligned} \tag{6}$$

Thus, values of θ and $r(0)$ are required to estimate $r_i(T)$. It follows that the spin-dependent part of the resistance (r_s) can be obtained by simply subtracting $r_i(T)$ from the measured value $r(T)$.

The method of calculating θ and $r(0)$ can be considered best under two classifications:

(a) Extremely dilute alloys where the anomalous resistivity would be expected to be negligible at $\frac{1}{3}\theta$.[17]

(b) More concentrated alloys where the anomalous resistivity extends above $\frac{1}{3}\theta$.

Case (a)

A value of $r(0)$, say $r_A(0)$ is assumed and the procedure for deriving θ as outlined in Sec. III.1 is carried out. The value of θ, say θ_1, so obtained is used to calculate a value of $r(0)$, say $r_c(0)$, in the following way: Using the measured values of $r(T)$ at two temperatures T_1 and T_2,[18] Eq. (6) is solved for $r(0)$ by noting

$$\frac{r(T_2)-r(0)}{r(T_1)-r(0)}=\frac{f(T_2/\theta)}{f(T_1/\theta)}$$

or

$$r(0)=\frac{n(\theta)r(T_1)-r(T_2)}{n(\theta)-1}, \tag{7}$$

where $n(\theta)=f(T_2/\theta)/f(T_1/\theta)$. The above procedure is carried out reiteratively until a value of θ is found which makes $r_A(0)$ and $r_c(0)$ equal. Since the value of θ is usually above the maximum temperature of resistivity measurement a value of $r(\theta)-r(0)$ was derived in the following manner. From Eq. (6) at temperatures T_1 and T_2, differences can be taken such that

$$\begin{aligned} r(\theta)-r(0) &= \frac{r(T_2)-r(T_1)}{f(T_2/\theta)-f(T_1/\theta)} \\ &= \frac{1-r(T_1)}{f(T_1/\theta)[n(\theta)-1]}. \end{aligned}$$

We now have $r(\theta)-r(0)$ and θ, and hence from Eq. (6), $r_i(T)$ and $r(0)$ can be evaluated and the separation of $r_s(T)$ carried out.

Case (b)

Since the spin-dependent term extends above $\theta/3$, the method of Kelly and MacDonald used in case (a) can no

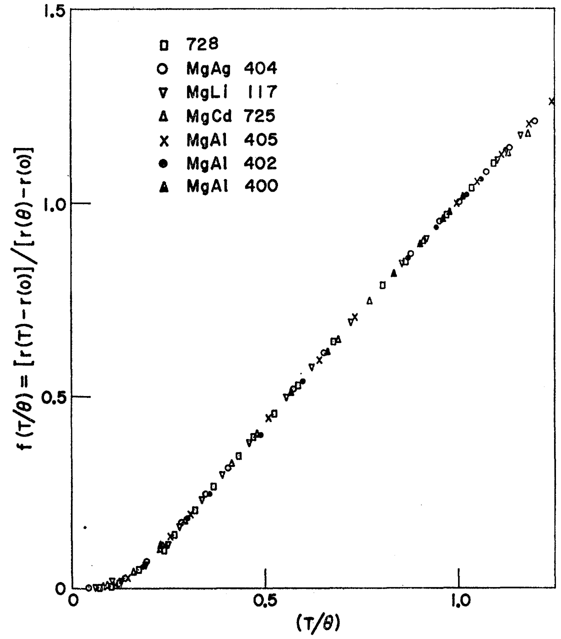


FIG. 4. The reduced thermal component of the resistivity plotted as a function of reduced temperature for the nontransition solute binary magnesium alloys.

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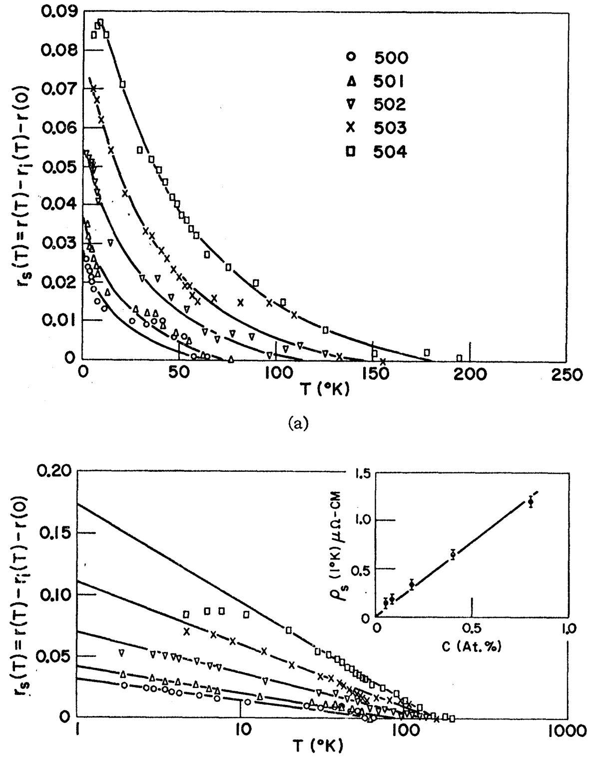
[17] The choice of $\frac{1}{3}\theta$ is made empirically.

[18] T_1 and T_2 are chosen to be 130 and 273°K, respectively, where $T_1=\theta/3$ and T_2 is the maximum temperature of measurement.

longer be used conveniently to estimate θ. In this case $r(0)$ is estimated by extrapolating a plot of $r(0)/[1-r(0)]$ versus $r(4.2)/[1-r(4.2)]$. The value of $r(4.2)/[1-r(4.2)]$ is a measure of concentration so that an extrapolation of the above curve can be made into the region of higher concentration and values of $r(0)$ determined from the known values of $r(4.2)$. With this information and using temperatures T_2 and T_3, where T_2 and T_3 are, respectively, 273 and 200°K, a value of $n'(\theta)$ is derived from Eq. (7) which is equal to

$$n'(\theta)=\frac{f(T_2/\theta)}{f(T_2/\theta)}=\frac{f(273/\theta)}{f(200/\theta)}=\frac{r(273)-r(0)}{r(200)-r(0)}$$

From known values of $r(0)$, $r(273)$, and $r(200)$, a value of θ can be estimated using a graph of $n'(\theta)$ as a function of θ. Again, θ is higher than the highest temperature of measurement; thus, $r(\theta)-r(0)$ is obtained from Eq. (6), since we already know $r(0)$, and $r(T)$ and $T(273.1°\mathrm{K})$. We now have values of θ, $r(\theta)$ and $r(0)$ so that $r_i(T)$ can be evaluated as before, and the separation of $r_s(T)$ made. Figure 5(a) shows $r_s(T)$ as a function of temperature for the various alloys listed in Table I.



(a)

(b)

FIG. 5. (a) The relative spin resistivity as a function of temperature for the various Mg-Mn alloys listed in Table I. (b) The reduced spin resistivity as a function of $\ln T$. The inset in the figure is the magnitude of spin resistivity at 1°K plotted as a function of concentration.

In recent theoretical work on the resistivity minimum in dilute alloys, Kondo[10] has carried out a calculation of the scattering of conduction electrons by magnetic impurities to the second Born approximation. He predicts that the resistivity due to spin scattering ρ_s should have the form

$$\rho_s=c\rho_M[1+(3zJ/E_f)\log T], \tag{8}$$

where z is the electron/atom ratio, E_f is the Fermi energy, J is the $s-d$ exchange integral, c is the concentration of paramagnetic ions (atom fraction), and $\rho_M=3\pi mJ^2S(S+1)(V/N)/2e^2hE_f$, where S is the spin value of the ion (assuming an S ground state), N/V is the number of atoms per unit volume, and e is the electronic charge. The term in $\log T$ is the "minimum" term, and the constant term ρ_M is the Yosida-Kasuya term.[19] In the presence of a cooperative magnetic interaction ρ_M will decrease below the Néel temperature and at absolute zero will have a constant value. In the preceding analysis of the resistivity curves, the constant term ρ_M has been included in the residual resistivity and has not been specifically allowed for above the Néel temperature.

Figure 5(b) shows a logarithmic plot of T versus $\rho_s(T)$ where it can be seen that good agreement with the theoretical prediction is obtained. The inset of the figure shows the concentration dependence of $\rho_s(1°\mathrm{K})$ as a function of concentration, and as is expected from Eq. (8), it varies linearly with c. From the slopes of the $\log T$ graph, values of J can be estimated which yield an average value of 0.76×10^{-12} erg, which is in fair agreement with the previously reported[20] value of 0.48×10^{-12} erg. This previously reported value was derived from magnetoresistivity and zero-field resistivity results in the region of the resistivity maximum. The calculation ignored the contribution due to the minimum in the presence of a maximum and would therefore be expected to underestimate a value for J.

IV. CONCLUSIONS

It has been shown that provided appropriate allowance is made for a change of the Grüneisen θ value in dilute alloys, containing nontransition element solutes, the temperature dependence of the thermal component of the electrical resistivity is independent of the nature or concentration of the solute. Furthermore, the adjustment of the θ value is all that is required to obtain agreement with Mathiessen's rule.

Assuming that transition element solutes only influence the lattice scattering above the temperature of

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the low-temperature resistance anomalies it is possible to separate, over an extended temperature range, the spin-dependent resistivity occurring in these alloys. The temperature dependence of the spin-dependent resistivity term is experimentally found to vary with $\log T$, and its magnitude found to vary linearly with paramagnetic impurity concentration in the solvent magnesium. Both of these experimental findings are in agreement with recent theoretical predictions of Kondo and yield a value of 0.76×10^{-12} erg for the $s-d$ exchange integral.

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Isotope Effect in Self-Diffusion in Palladium

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The diffusion of Pd^{103} in single crystals of palladium has been measured over the temperature range of 1050–1500°C by the tracer-sectioning technique. The results are

$$D=0.205_{-0.04}^{+0.05}\exp[-(63\,600\pm650)/RT]\mathrm{cm}^2/\mathrm{sec}.$$

Four measurements of the isotope effect for diffusion of Pd^{103} and Pd^{112} in each of four single crystals of palladium have been made between 1450 and 1500°C. The measured isotope effect E_β as defined by the equation $E_\beta=(1-D_\beta/D_\alpha)/[1-(m_\alpha/m_\beta)^{1/2}]$, where D_β/D_α and m_α/m_β are the ratios of the diffusion coefficients and masses of the two isotopes α and β was found to be 0.8134 ± 0.0424. This value is consistent only with diffusion by the vacancy mechanism, and indicates that the translational kinetic energy of the activated state in the jump direction is possessed entirely by the jumping atom as it crosses the saddle point.

INTRODUCTION

It is generally agreed that diffusion in crystals takes place by a series of jumps of individual atoms from one site to another throughout the crystal. For random jumps, the diffusion coefficient D for isotropic diffusion is given by

$$D=\tfrac{1}{6}\Gamma r^2, \tag{1}$$

where Γ is the jump frequency and r is the jump distance. If the direction of a given jump depends on the direction of a previous jump, then[1–3]

$$D=\tfrac{1}{6}\Gamma r^2 f, \tag{2}$$

where the correlation factor f takes into account the correlation between the directions of successive atom jumps. For self-diffusion, f is a geometrical factor determined only by the crystal lattice and the diffusion mechanism, and it can be calculated mathematically.[3–5] For impurity diffusion in an isotropic crystal, f depends on the jump frequencies of both the solute and solvent species.[2,6,7] For impurity diffusion by the vacancy mechanism, $0<f<1$.

Since f depends only on the mechanism of diffusion, the crystal structure and, in the case of impurity diffusion, on the relative jump rates, much information can be obtained about diffusion in crystals if we can measure f. For either impurity diffusion or self-diffusion, f can be obtained from accurate measurements of the relative diffusion rates of two different isotopes of the same element. Schoen,[8] and later Tharmalingam and Lidiard,[9] derived the relation

$$(1-D_\beta/D_\alpha)=(1-\Gamma_\beta/\Gamma_\alpha)f_\beta, \tag{3}$$

where the D's and Γ's are the diffusion coefficients and jump frequencies of the two isotopes α and β of the same chemical element. Using the relation $\Gamma\propto m^{-1/2}$, we have

$$\Gamma_\beta/\Gamma_\alpha=(m_\alpha/m_\beta)^{1/2}, \tag{4}$$

for a mechanism involving the motion of only one atom, and

$$\frac{\Gamma_\beta}{\Gamma_\alpha}=\left[\frac{(n-1)m+m_\alpha}{(n-1)m+m_\beta}\right]^{1/2}, \tag{5}$$

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