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Electrical Resistivity and Deviations from Matthiessen's Rule in Dilute Alloys of Aluminum, Cadmium, Silver, and Magnesium†

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Absolute values of the electrical resistivity of polycrystalline silver, aluminum, cadmium, and magnesium and over 20 dilute binary alloys of these metals with different solute concentrations have been measured from 1.5 to 300 °K. From the resistivity data, deviations Δ from Matthiessen's rule have been evaluated for the alloys. Deviations with positive as well as negative sign have been observed at temperatures above 50 °K. These deviations, for all except the hcp alloys of cadmium containing magnesium as a solute (*Cd*-Mg alloys), can be explained in terms of a two-band contribution, which can only be positive, and an interference term between the scattering of electrons by lattice vibrations of the host atoms and the excess potential due to the vibrating impurities, which can have either sign. The deviations for *Ag*-Cd, *Ag*-Mg, *Ag*-Al, and *Al*-Mg alloys increase linearly with temperature and those for *Al*-Ag, *Cd*-Ag, and *Mg*-Al decrease linearly with temperature in this range. Combined with published data for *Mg*-Ag alloys, these results are in excellent qualitative agreement with the predictions of Bhatia and Gupta, who showed that the interference term should be important at high temperatures and should change sign when the ions on the host and impurity sites are interchanged. This agreement is further strengthened by comparison of the slope $d\Delta/dT$ of the experimental results for the alloys of magnesium and aluminum with a semiquantitative calculation by Gupta. Near 250 °K Δ is negative and $d\Delta/dT$ is temperature dependent for *Cd*-Mg alloys, and further work is required to clarify this result. Below about 50 °K deviations for all alloys are positive, and the various contributions are discussed. The precise resistivity results obtained over a wide temperature range extend our knowledge of deviations from Matthiessen's rule, but the complexity of the scattering processes makes a detailed comparison with theory difficult, particularly at low temperatures.

INTRODUCTION

The total electrical resistivity of a dilute alloy may be written as

$$\rho(T)=\rho_i(T)+\rho_0+\Delta(T) \quad , \tag{1}$$

where ρ_i is the resistivity that an ideally pure and perfect crystal of the host metal would have at temperature T, ρ_0 is the temperature-independent resistivity due to static defects, and Δ is a term that represents the deviations from Matthiessen's rule. If we confine our attention to alloys in which the impurity content is less than 2%, there is reason to believe from Mössbauer experiments, for example,[1,2] that, in general, the phonon spectrum is little changed from that of the pure metal, and from de Haas–van Alphen measurements,[3] that the electronic structure of a metal is not greatly changed by the impurity. Under these circumstances, we would expect that contributions to Δ that might arise from a deformed phonon spectrum, or from changes in the Fermi surface, would be negligible. Omitting also effects due to magnetic interactions, the other important contributions to Δ that have been considered by various authors are as follows:

(i) Inelastic scattering of the electrons by the excess potential of the *vibrating* impurity ions.[4,5] The impurity potential may be modified by the strain due to the thermal vibrations of the impurity,[6] considerably enhancing this effect.

(ii) An interference term is to be expected between the scattering by the vibrating impurities and the host ions.[7,8]

(iii) Even if unique relaxation times can be separately defined for the phonon and impurity scattering mechanisms, they may vary differently over the Fermi surface.[9] Such different anisotropies will give rise to positive values of Δ. This contribution is often analysed in terms of the two-band effect.[10,11]

Deviations from Matthiessen's rule have been measured by several experimenters (see, for example, the review by Gerritsen[12] and subsequent experiments[10,13–21]) and various behaviors have been observed at low temperatures. However at temperatures $T\sim\Theta_D$, the Debye temperature of the lattice, the deviations are often linear in T and may be either positive or negative in sign. Bhatia and Gupta[8] were the first to draw attention to the fact that the interference term (ii) would be substantial at these temperatures and would have the observed characteristics at high temperatures. Of course, some of the other deviations may persist to high temperatures but those that do are expected to be positive. A more stringent test for the existence of the interference term was also proposed by Bhatia and Gupta. They noted that in an alloy with host ions of metal *A* and impurity *B* the slope $d\Delta/dT$ for the interference contribution should usually have the opposite sign from that for the complementary alloy with impurity *A* in host metal *B*. With this test in mind, we prepared specimens of all the binary alloy systems for which the solid solubility data showed that dilute *AB* and *BA* specimens could be homogenized and annealed without mixed phases appearing.

EXPERIMENTAL

Silver, aluminum, cadmium, and magnesium were used for the preparation of the specimens. The first three were obtained from Consolidated Mining and Smelting Co. of Canada and were of 59 grade purity. The magnesium (from Johnson Matthey, and Mallory Ltd., Canada,) was spectrographically standardized metal with < 14-ppm impurity.

The pure aluminum was supplied in rod form, but pure silver and cadmium rods were made by melting freshly cleaned pellets in evacuated ($<10^{-5}$ Torr) sealed quartz tubes. The preparation method for rods of each of the alloys was similar except that an atmosphere of about 10 Torr of hydrogen gas was sealed in the quartz tube to reduce any oxide that might form whenever magnesium was the solute metal. Also, because aluminum can pick up traces of silicon from quartz at high temperatures, a small tube of high-purity graphite with graphite stoppers at each end was placed inside the quartz tube to hold the weighed amounts of metal for alloys containing aluminum. The graphite was outgassed at 1000 °C before use. Pyrex containers were used for cadmium and its alloys which all became liquid at 450 °C or lower. For each system, master alloys were first made and homogenized by shaking periodically during a melt period lasting several hours, and then they were annealed just below the solidification temperature for several more hours. The more dilute alloys, made by melting together weighed quantities of master alloy and solvent metal, were cooled after shorter periods.

These rods, which were about 6mm in diam, were reduced to 1.5 mm diam by drawing through steel dies. After each three or four reductions the rods were etched to remove surface contamination and sometimes annealed to remove cold work. The 1.5-mm rods were reduced to 0.5-mm-diam wires by drawing through diamond dies. Microscopic examination after this procedure showed no surface irregularities on the specimens. A traveling probe arrangement was used to measure the resistance at room temperature of each 10 cm length of 1 m of Al wire and 1 m of an Al–2%-Mg-alloy wire prepared in this way. The standard deviations of the resistance values from the mean for each of these wires was 0.07%, which indicates that no appreciable error is introduced in the resistivity results by the assumption that the density and cross section of the wires were uniform and that the alloy was homogeneous.

The 0.5-mm-diam wires were annealed as shown in Table I. Separate close-fitting containers were made, in which to anneal each *Ag*-Cd, *Al*-Mg, and *Cd*-Mg [22] wire, in order to minimize the preferential evaporation of the high vapor pressure component in these alloys.

The pure magnesium and *Mg*-Al alloy specimens were prepared by Dow Chemical Co. from sublimed magnesium that was "at least 99.98% pure after fabrication." They were supplied as slightly nonuniform 0.035-in.-diam wires which were drawn through the 0.032-in. diamond die to produce uniform, smooth wires prior to annealing.

In Table II the solute concentration is shown for each of the alloy specimens. Possibly the best indication of the solute concentration in a dilute binary alloy is afforded by the residual resistivity. In this regard the *Ag*-Al, *Al*-Ag, *Cd*-Mg, *Cd*-Ag, and *Mg*-Al alloys presented no difficulty. The residual resistivity of each specimen was proportional to the solute concentration determined either from the weights of the constituents during preparation or, for the *Mg*-Al alloys, from spectrographic analyses supplied by the manufacturer, and the values agreed with published data. Some preferential evaporation was expected from the *Ag*-Cd, *Ag*-Mg, and *Al*-Mg alloys, so chemical analyses of these alloys were obtained. The results of these analyses gave agreement between the measured residual resistivities for the most concentrated specimens (1- and 2-at.% solute) and the published values. For the lower concentrations the uncertainty in the chemical analyses was large, so the solute concentrations were determined from the residual resistances.

An x-ray microanalysis was performed with an electron probe[23] on all specimens except the *Cd*-Ag and the *Cd*-Mg alloys. Although self-absorption of the x rays in the specimens limited the accuracy of concentration determinations in our dilute alloys by this method, specimen homogeneity was carefully checked. Profiles were taken across diameters at various positions in the wire near the places the resistivity specimens were taken from. Fluctations in the solute concentration were never more than 10% of the average concentration in the 1 and 2% alloys and typically they were more aften about 5%. Variations in the average concentration from one

TABLE I. Annealing treatment of the specimens.

Specimen	Temperature (°C)	Time (h)	Atmosphere	Remarks
pure Ag	600	6	$< 10^{-5}$ Torr	$r = 2000$[a]
	600	6	10 Torr H_2	$r = 2000$
Ag-Cd	500	12	$\sim 10^{-6}$ Torr	close-fitting quartz containers
Ag-Mg	500	12	10 Torr H_2	close-fitting quartz containers
Ag-Al	550	12	$< 10^{-5}$ Torr	
pure Al	400	12	$\sim 10^{-6}$ Torr	$r = 4000$
Al-Mg	400	12	10 Torr H_2	close-fitting Pyrex container
Al-Ag	400	12	$\sim 10^{-6}$ Torr	
Pure Cd	125	12	$\sim 10^{-6}$ Torr	$r = 13\,500$
Cd-Ag	125	12	10^{-6} Torr	close-fitting Pyrex container
Cd-Mg	125	12	10^{-6} Torr	close-fitting Pyrex container
pure Mg	350	8	10 Torr H_2	$r = 700$
Mg-Al	350	8	10 Torr H_2	

[a] $r \simeq R(293)/R(4)$.

profile to another within the same specimen were much smaller than these values.

The temperature dependence of the resistivities was measured in a cryostat similar to the one described by White and Woods[24] except that the specimen chamber was 11 in. long and $2\frac{1}{2}$ in. in diam. Specimens, up to six at a time, were mounted on a Tufnol board $8\frac{1}{2}$ in. long, 2 in. wide, and $\frac{1}{2}$ in. thick. Six channels, $\frac{1}{4}$ in. deep and slightly wider than the specimens, were cut in one face of the Tufnol, and the ends were machined to $\frac{1}{4}$ in. thick so that the specimen wires could be firmly held by sharp potential clips of beryllium-copper at the ends of the channels. As the apparatus was cooled the Tufnol contracted more than the metal, so the specimens were not strained. After the resistance measurements were done the distance between the clip marks, which was about 20 cm, was measured at room temperature on each specimen with an uncertainty of 0.01 mm. The specimens were then cut at the clip marks and weighed on a microbalance. The cross-sectional areas were calculated with an uncertainty of less than 0.1% using accurate alloy densities obtained from crystallographic data.[25]

The specimen chamber contained helium at a pressure of a few Torr so that all specimens were kept at the same temperature within ±0.01 °K during a set of measurements which typically took about 20 min. A pure metal specimen was included with each set of alloys so that $\rho_i(T)$ was obtained simultaneously with $\rho(T)$ for the alloys. A platinum resistance thermometer and a germanium thermometer inserted in wells in a copper block attached to the back of the Tufnol board were used for temperature measurement. The platinum thermometer has been calibrated by the National Research Council of Canada in terms of the 1960 International Practical Temperature Scale from 90 to 523 °K with a calibration uncertainty of 2 mdeg C and in terms of the N.B.S. 1955 Provisional Temperature scale from 20 to 90 °K. The germanium thermometer was calibrated by us from 2 to 5 °K against the vapor pressure of He^4 using the 1958 temperature scale and the two calibrations were joined between 5 and 20 °K with the help of a calibrated germanium thermometer (guaranteed to ±0.1 °K) obtained from Solitron Devices, Inc. The isolating potential comparator[26] used for measuring the thermometer resistances permitted display of its output signal on a chart recorder so that temperature drifts in the specimen chamber could be continuously monitored.

A current of either 20 or 50 mA was maintained through the specimens and a standard 0.01-Ω resistor connected in series with them during experimental runs. Occasionally, the current was interrupted to test for errors due to heating effects but none were noticeable. At the lowest temperatures, when more than 50 mA was required for residual resistance measurements of the pure specimens, the current through the rest of the specimens was interrupted. Standard techniques were employed to minimize the effect of thermal emf's in the leads and measuring equipment; a potentiometer and galvanometer amplifier system were used with which a change of 10^{-8} V could be detected. With this system, it was possible to determine resistance values to within ±0.005% or 1 μΩ, whichever was greater.

DATA ANALYSIS

Resistivity measurements are needed for an alloy sample and a sample of the pure host metal, in which it is assumed the deviations from Matthiessen's

TABLE II. Ice-point resistivity and residual resistivity of the specimens.

Sample[a]	$\rho(273.2)$ ($\mu\Omega$ cm)	ρ_0 ($\mu\Omega$ cm)
Ag 1	1.472	0.0008
Ag 2	1.468	0.0008
Ag-0.10%Al	1.707	0.1836
Ag-0.88%Al	3.185	1.620
Ag-1.93%Al	5.223	3.578
Ag-0.07%Mg	1.533	0.0328
Ag-1.09%Mg	2.038	0.5399
Ag-1.61%Mg	2.239	0.7949
Ag-0.04%Cd	1.487	0.0119
Ag-0.48%Cd	1.642	0.1605
Ag-1.43%Cd	1.984	0.4761
Al	2.430	0.0007
Al-0.13%Mg	2.485	0.0487
Al-0.61%Mg	2.703	0.2355
Al-1.75%Mg	3.205	0.6810
Al-0.06%Ag	2.502	0.0707
Al-0.18%Ag	2.625	0.1950
Cd 1	6.986	0.0020
Cd 2	6.929	0.0022
Cd-0.2%Ag	7.030	0.0704
Cd-1.0%Ag	7.068	0.3002
Cd-2.0%Ag	7.138	0.5468
Cd-0.75%Mg	7.129	0.2217
Cd-1.5%Mg	7.417	0.4960
Cd-3.0%Mg	7.832	0.9920
Mg	4.108	0.0065
Mg-0.22%Al	4.555	0.4692
Mg-0.99%Al	6.108	2.055
Mg-1.90%Al	7.919	3.950

[a]All solute concentrations for the alloy specimens are given in at. %

rule are negligible, in order to calculate the deviations in the alloy sample. If we designate the pure and alloy samples by subscripts P and A, respectively, we may rewrite Eq. (1) as

$$\Delta(T)=[\rho_A(T)-\rho_A(0)]-[\rho_P(T)-\rho_P(0)] \quad . \qquad (2)$$

The resistance-temperature data from the experiments have, following usual practice, been converted to resistivity data for use in the above expression using the values of the specimen form factors, f(= length/cross-sectional area) measured at room temperature (293 °K). Since f is slightly temperature dependent, this procedure leaves a small correction to be applied to the resistivities before comparing them with data from specimens for which the geometry was determined at a different temperature. The correction to Δ may, however, amount to several precent, and thermal-expansion data have been tabulated by Corruccini and Gniewek[27] with which it can be evaluated for a number of metals. They list values of

$$\alpha(T)=10^5[L(293)-L(T)]/L(293) \quad ,$$

the linear contraction relative to 293 °K, in terms of which the correction

$$\Delta_{ex}=10^{-5}\rho_A(0)[\alpha(0)-\alpha(T)] \qquad (3)$$

should be added to Δ calculated from Eq. (2). This form of the correction has been derived with the assumptions that $\rho_P(0)=0$ and that the expansion of the dilute alloys involved here, for which data are not available, is the same as that of the pure metals.

It has been pointed out[10,28] that in order to relate the deviations from Matthiessen's rule to the electron scattering processes, the various resistivities $\rho_A(T)$, $\rho_A(0)$, and $\rho_P(T)$ should be compared at the same atomic volume. This means that $\rho_P(T)$ should be corrected at all temperatures for a fixed change in atomic volume that is produced by alloying. Also, $\rho_A(0)$ should be corrected for change due to thermal expansion of the atomic volume as the temperature is raised. Accurate crystallographic data exist from which the volume change may be computed for each of these corrections, but it is then necessary to relate these volume changes to the changes in $\rho_P(T)$ and $\rho_A(0)$ that they will produce. Measurements under pressure have been made,[29] mostly at room temperature although a few have been made at helium temperatures,[30] from which the volume dependence of the measured resistivity may be calculated. Using these data it is possible to estimate the influence of alloying on the ideal resistivity of the metals used in the present investigation but we believe that an overestimate of the corrections to be applied to Δ is obtained in this way. Electrical resistivity depends on the lattice spectrum, the electronic band structure, and the atomic pseudopotentials of a metal, which factors are certainly affected quite differently by the addition of impurities on localized sites and the application of uniform pressure. We have not applied this correction to our results, although it may be substantial near room temperature where ρ_P is large; we prefer to await the time when a more clear theoretical picture may allow a calculation of this effect. It may be possible to apply the correction to $\rho_A(0)$ with greater confidence but, unfortunately, data under pressure exist for only three of the seven alloy systems investigated here and the correction for two of them can be inferred[31] both from measurements near 300 °K and near 4 °K. Quite different values are obtained for the correction from the two sets of data, which probably reflects the uncertainties in the way the data are used rather than in the experimental information. In this situa-

TABLE III. The ideal resistivity ratio $\rho_i(T)/\rho_i\,(273.2)$ between 10 and 295 °K for the pure specimens.

T (°K)	Al	Ag	Mg	Cd
10	1×10^{-5}	0.0001	0.0002	0.0017
20	0.0003	0.0022	0.0017	0.020
30	0.0019	0.0126	0.0060	0.0518
40	0.0074	0.0362	0.0167	0.0897
50	0.0195	0.0702	0.0358	0.1288
60	0.0394	0.1105	0.0633	0.1686
70	0.0669	0.1534	0.0977	0.2081
80	0.1008	0.1973	0.1370	0.2471
90	0.1397	0.2413	0.1799	0.2861
100	0.1819	0.2849	0.2248	0.3248
120	0.2727	0.3706	0.3173	0.4016
140	0.3675	0.4550	0.4105	0.4786
160	0.4637	0.5381	0.5030	0.5551
180	0.5600	0.6205	0.5938	0.6324
200	0.6555	0.7022	0.6832	0.7099
220	0.7505	0.7837	0.7712	0.7881
240	0.8450	0.8650	0.8579	0.8673
260	0.9384	0.9465	0.9439	0.9469
295	1.1021	1.0891	1.0926	1.0894

tion we have chosen also not to apply this correction to our results; it may be noted that it would be largest where the thermal expansion is greatest but, in some cases, will be opposite in sign to the correction for alloying.

RESULTS

Values of the resistivity measured at 273.2 °K, $\rho(273.2)$, and below 4.2 °K, ρ_0, are given in Table II for each specimen. In Table III, the ratio of the ideal resistivity to that at the ice point is shown for several temperatures for the pure Al, Ag, Mg, and Cd specimens. The values of the ideal resistivity were obtained from a computer interpolation and checked with smooth graphs drawn through the experimental values of $\rho - \rho_0$. The ice-point resistivities are compared in Table IV with some values from the literature for these metals. It is, perhaps, surprising that "accepted" values even for the cubic metals are based on a very few measurements, some of which are now quite old and of limited accuracy. While reasonable agreement exists among the various values for Ag and Al, the situation is more complicated for the anisotropic hexagonal metals. Mg exhibits a minimum in its resistivity near 4 °K,[34] which makes the choice of a value for ρ_0 difficult; in our specimen $\rho(1.6)/\rho(4) = 1.015$, and we chose $\rho_0 = \rho(4)$ although any reasonable choice of ρ_0 would give the same value for $\rho_i(273)$ within experimental error. The interesting comparison is between the ice-point resistivities measured by different observers[14,17,19] on extruded specimens of small cross sections, which are consistent with one another, and the value determined by Nichols[33] from measurements on $\frac{1}{2}$-in.-diam single crystals and a polycrystalline specimen. It appears that the thin extruded specimens contained crystallites with a preferred orientation that was very nearly the same in each case. Fewer measurements have been made on cadmium, but $\rho_i(273)$ for two specimens measured here differed by 0.8% although they were prepared from the same starting material. Enough of the rod remained from which specimen Cd 2 had been taken to permit us to draw two more specimens. These were annealed quite differently and had residual resistivities that differed by 50%, but for both $\rho_i(273)$ was within 0.2% of the value for Cd 2. None of these values agrees with that to be expected for randomly oriented polycrystalline cadmium, although the temperature dependence of the ideal resistivity agrees within experimental error with previous data.[34]

All measurements reported here were made after a long enough annealing period that $\rho(273)$ was stable, and the temperature of the mounted specimens was cycled between room temperature and 80 °K several times to further check the reproducibility of the readings before collecting resistivity-temperature data. The Δ values were obtained and are plotted in Figs. 1–8 without smoothing by using ρ_P values measured on the pure specimen mounted beside the alloy in question and measured at the same temperatures.

DISCUSSION

If deformation of the phonon spectrum has any

TABLE IV. Comparison of the ideal ice-point resistivity of the pure specimens with some values from the literature.

Metal	Ref.	$\rho_i(273.2)$	Specimen
Al	32	2.44	
	This work	2.429	
Ag	32	1.47	
	This work	1.471	Ag 1
		1.469	Ag 2
Cd	33	7.1	a
		6.8	b
	This work	6.98	Cd 1
		6.93	Cd 2
Mg	14	4.11	c
	17	4.16 ± 0.02	c
	19	4.04	c
	This work	4.101	c
	33	3.93	d

[a] Measured on polycrystalline specimens.

[b] Calculated from single-crystal data.

[c] Measured on thin extruded polycrystalline specimens.

[d] Calculated from measurements on $\frac{1}{2}$-in.-diam single crystals assuming ρ_0 is negligible.

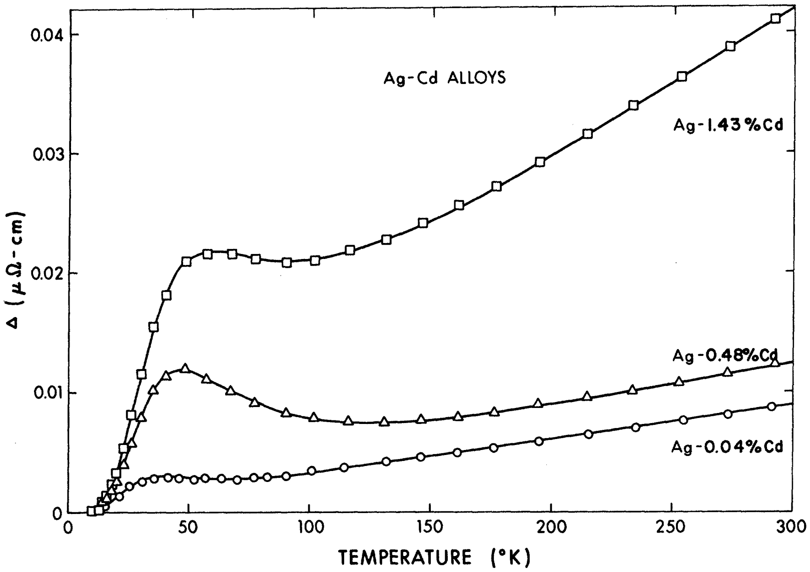

FIG. 1. Temperature dependence of deviations from Matthiessen's rule in silver-cadmium alloys.

substantial effect on the deviations from Matthiessen's rule, it should be particularly evident in those alloys where the mass ratio of the two components is large. Our alloys may be divided into three groups: (a) *Ag*-Al, *Ag*-Mg, and *Cd*-Mg, in which the solute atoms are light and may have a local mode associated with them. As the temperature is increased, a change in slope of the Δ-T curves to a more positive value might be expected[18] for these alloys near 200 °K. (b) *Al*-Ag in which a quasilocal mode may be associated with the heavy solute atom. In this case according to Kagan and Zhernov,[7] a broad maximum may occur below the temperature associated with this mode, which for *Al*-Ag is $T^* \simeq 130$ °K. Alloy systems such as *Mg*-Cd and *Mg*-Ag, which belong in this group and have $T^* \sim 100$ °K, have been examined by other experimentalists.[17,19] (c) The other four alloy systems in which the masses of the two components differ only slightly. Comparison of the Δ-T curves for these alloys shows no clear differences between the groups. On the other hand, Panova *et al.*[20] report an effect in *Mg*-Pb alloys from a quasilocal mode. We conclude that modifications of the phonon spectrum in dilute alloys containing only magnesium, cadmium, silver, or aluminum are not large enough to produce substantial deviations from Matthiessen's rule. This is consistent with the conclusion reached by Damon and Klemens[18] after a study of gold alloys.

The observed deviations can then be attributed

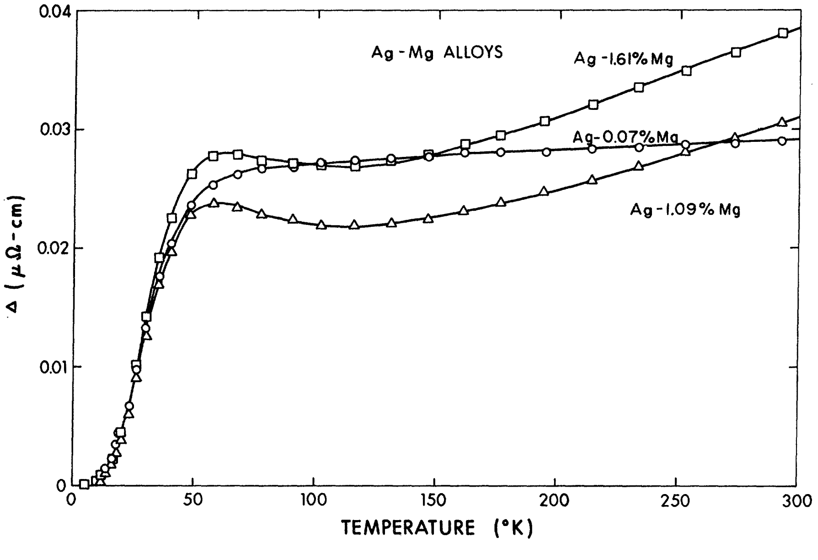

FIG. 2. Temperature dependence of deviations from Matthiessen's rule in silver-magnesium alloys.

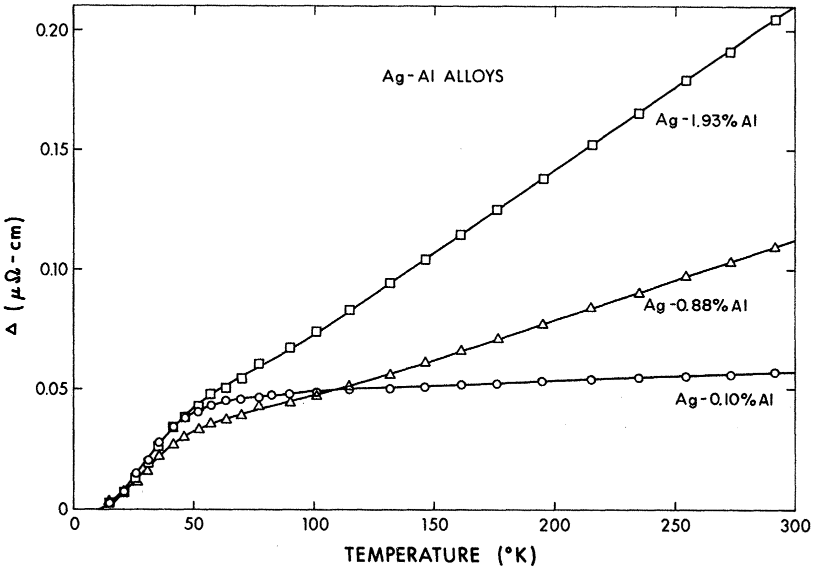

FIG. 3. Temperature dependence of deviations from Matthiessen's rule in silver-aluminum alloys.

to the three effects enumerated in the Introduction. Although it is not possible with present knowledge to entirely separate contributions to the observed values through their temperature dependencies, some illuminating conclusions can be reached.

At low temperatures, only the deviations Δ_1 due to inelastic scattering from impurities and Δ_3 from the two-band effect are expected to be important. Δ_1 may have a temperature variation between T^2 and T^4, but it is always proportional to c, the impurity concentration, whereas $\Delta_3 \propto \rho_i$ and independent of c when $\rho_0 \gg \rho_i$. Our results cannot be explained by either effect alone, but we would require more specimens of each alloy system to separate the contributions of Δ_1 and Δ_3 and establish their temperature dependences as Damon, Mathur, and Klemens[21] did for some gold alloys.

As the temperature is raised, Δ_1 will pass through a maximum and become negligible when the product of the lifetime of the electron states and the dominant phonon frequency is no longer greater than unity. The behavior of Δ_3 is complicated to evaluate

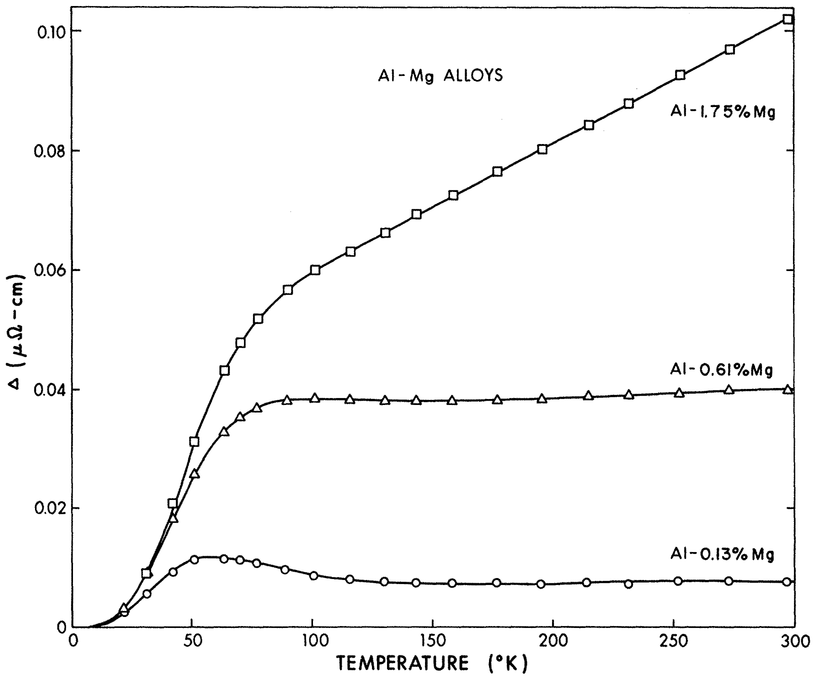

FIG. 4. Temperature dependence of deviations from Matthiessen's rule in aluminum-magnesium alloys.

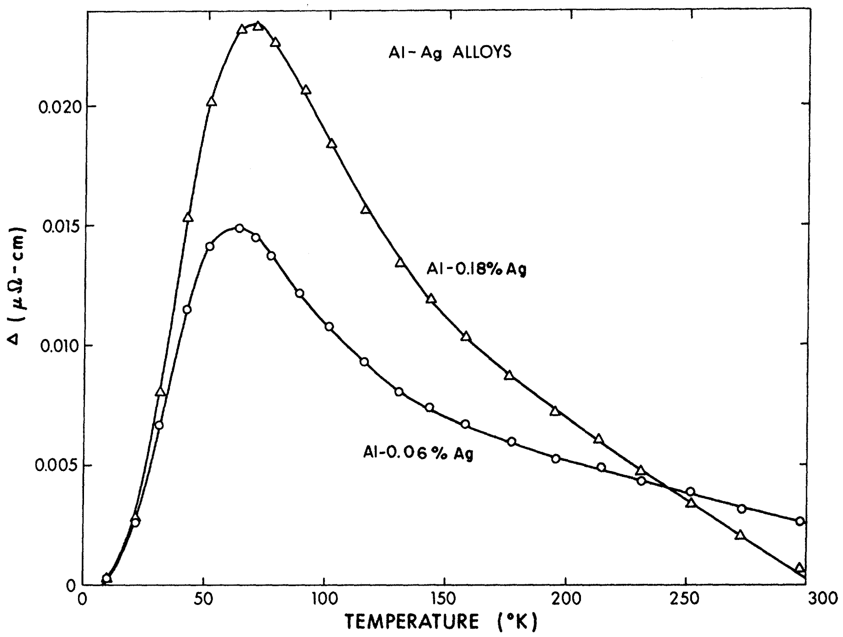

FIG. 5. Temperature dependence of deviations from Matthiessen's rule in aluminum-silver alloys.

until $\rho_i \gg \rho_0$ when it becomes independent of temperature and proportional to ρ_0. Two groups of authors[7,8] independently have shown that Δ_2, which arises from the interference between elastic scattering by impurities and by the phonon spectrum of the host lattice, is small if only small-angle scattering is included in the calculation. However, Bhatia and Gupta included scattering at all angles and found that umklapp processes raised Δ_2/ρ_0 to a value of the order of a few percent for $T \sim \theta$. Also, Δ_2 has the same temperature variation as ρ_i and $\Delta_2 \propto c$ for $c \ll 1$. Further, they noted that Δ_2 could be either positive or negative depending on the sign of the difference of the pseudopotential matrix elements for the impurity and the host atoms. This is in contrast to the other contributions to Δ which are

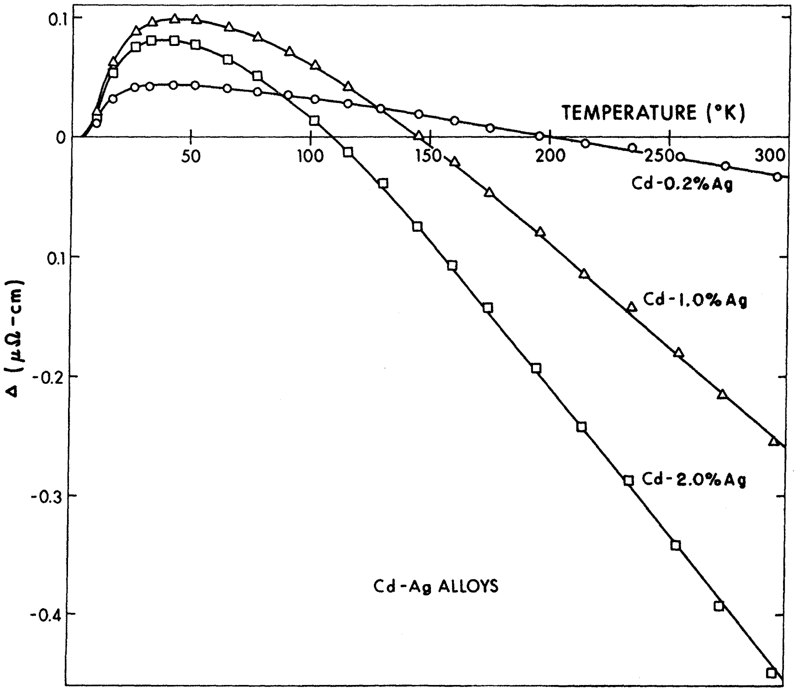

FIG. 6. Temperature dependence of deviations from Matthiessen's rule in cadmium-silver alloys.

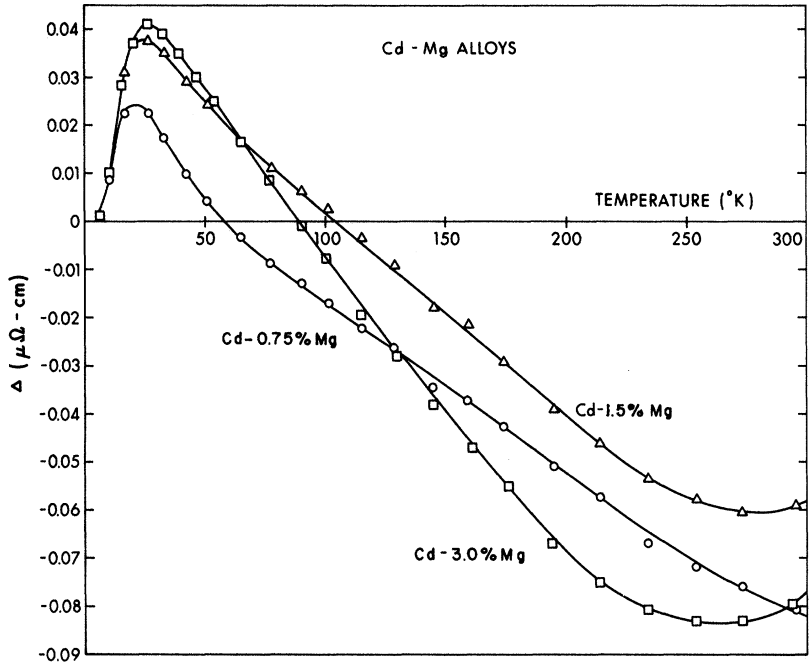

FIG. 7. Temperature dependence of deviations from Matthiessen's rule in cadmium-magnesium alloys.

essentially positive.

The temperature at which $\rho_i \simeq \rho_0$ is shown in Table V for each specimen, from which it is evident that Δ_3 will be at least slightly temperature dependent everywhere within the range of measurement for most of the alloys. However, not only must Δ_3 be positive everywhere, but $d\Delta_3/dT$ can only be negative if the conductivities of the two bands vary in a special way with temperature. This is not usually envisaged, and in any case there is no reason to expect $d\Delta_3/dT$ to change sign whenever the host and impurity atoms exchange roles. Since an exchange of host and impurity atoms (from alloy A-B to the complementary alloy B-A) does change the sign of Δ_2 but leaves its magnitude proportional to T at high temperatures, the sign of $d\Delta_2/dT$ will change and this affords a method of experimentally determining the presence of Δ_2.

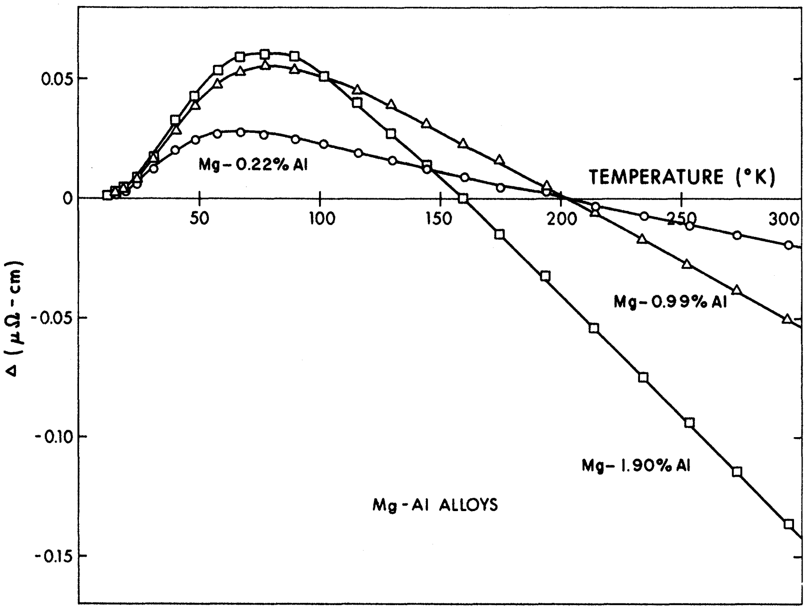

FIG. 8. Temperature dependence of deviations from Matthiessen's rule in magnesium-aluminum alloys.

TABLE V. Values of T for which $\rho_0 \simeq \rho_i$, of the slope $(10^4/c)d\Delta/dT$, and the temperature $T^\dagger$ above which it achieves the values shown.

Specimen	T(°K) at which $\rho_0 \simeq \rho_i$	$(10^4/c)d\Delta/dT$ ($\mu\Omega$ cm/°K at. %)	$T^\dagger$ (°K)
Ag-0.04% Cd	27	7.0	90
Ag-0.48% Cd	60	0.7	170
Ag-1.43% Cd	110	0.8	170
Ag-0.07% Mg	35	~ 1	100
Ag-1.09% Mg	120	0.6	180
Ag-1.61% Mg	160	0.5	180
Ag-0.10% Al	63	~ 4	100
Ag-0.88% Al	300	3.8	120
Ag-1.93% Al	>300	3.6	100
Al-0.13% Mg	50	...	...
Al-0.61% Mg	80	~ 0.3	160
Al-1.75% Mg	120	1.2	100
Al-0.06% Ag	55	− 4.5	190
Al-0.18% Ag	75	− 3.7	190
Cd-0.2% Ag	15	−17	100
Cd-1.0% Ag	27	−17	150
Cd-2.0% Ag	37	−13	150
Mg-0.22% Al	75	− 9.1	90
Mg-0.99% Al	160	− 5.6	120
Mg-1.90% Al	270	− 5.5	140
Mg-Ag 1[a]	70	− 4.9	150
Mg-Ag 2[a]	90	− 1.6	150
Mg-Ag 3[b]	130	− 2.1	100

[a] Specimens from Ref. 17. Data estimated from their impurity-resistivity–versus–temperature graphs.

[b] Specimens from Ref. 19.

The eight alloy systems we have investigated consist of three complementary pairs and two other systems whose complementary alloys have been investigated by other authors. The maximum in Δ observed near 50°K by some other investigators, but not in all alloys, is clearly evident in some, but not all, of the alloys measured here. We hesitate to attribute it mainly to a two-band effect as Dugdale and Basinski did because of the difficulty of separating the contributions to Δ below 50 °K and because for some of the alloys Δ becomes negative at higher temperatures and cannot then be accounted for by a two-band model. On the other hand, at high enough temperatures the slope of the Δ-T curves becomes constant for all except possibly the *Cd*-Mg alloys. An examination of Table V reveals that the quantity $(1/c)d\Delta/dT$ in this temperature range is positive for *Ag*-Cd, *Ag*-Mg, *Ag*-Al, and *Al*-Mg alloys and is negative for *Cd*-Ag, *Mg*-Ag, *Al*-Ag, and *Mg*-Al alloys. It may be noted, also, that if the most dilute alloy is omitted in each case, then $(1/c)d\Delta/dT$ is almost constant for each alloy system. These are characteristics to be expected of Δ_2 whereas Δ_3, particularly for the less dilute alloys where $\rho_i \gg \rho_0$ is not satisfied within the measurement range, should exhibit a more complicated behavior. An additional term in the observed Δ that is proportional to T but that varies less rapidly than linearly with c could account for the high values of $(1/c)d\Delta/dT$ in the very dilute alloys. The correction for change in atomic volume on alloying, if it were made, is in the right direction to improve the agreement in magnitude of $(1/c)d\Delta/dT$ for the complementary systems, except possibly in the case of *Ag*-Al and *Al*-Ag where the agreement is already good and the correction is relatively small. Also it should be noted that each atomic pseudopotential depends on the environment of the atom,[35] so that in addition to the sign change there will be some change in the factors comprising Δ_2 when the host and impurity atoms are interchanged. In this connection, Gupta[36] has made some semiquantitative estimates, according to which $\Delta_2(273)/c$ and $(1/c) \times d\Delta_2/dT$ should be twice as great for *Mg*-Al as for *Al*-Mg alloys. Considering the approximations involved in making the estimates, the agreement with the experimentally determined ratio of the slopes (which is $\simeq 5$) is satisfying.

The results above 50 °K for the alloys of cadmium and magnesium are more puzzling because, although the deviations for Cd-Mg alloys become negative indicating a large contribution from Δ_2, the slope of the Δ-T curve is negative for both *Cd*-Mg and *Mg*-Cd[17,19] alloys. Also, $d\Delta/dT$ for *Cd*-Mg alloys appears to change sign near the highest temperatures at which measurements were made, which is unexpected on the basis of the presently known contributions to Δ. In light of the uncertainty of ρ_i for Cd, we evaluated Δ for all the Cd alloys using extreme values of ρ_i; but although the magnitude of the deviations was affected in obvious ways, the sign of $d\Delta/dT$ could not be changed. The order-disorder temperature of $MgCd_3$ is in the range 80–94 °C, and it is possible that the peculiar resistive behavior of the *Mg*-Cd alloys arises from some ordered structure that might have formed during the annealing procedure. We believe, however, that it more likely arises from different textures – grain structures and degrees of preferred crystallite orientation – in different specimens. This could also account for the different ice-point resistivities observed for the pure specimens. Further investigations of these alloys will be necessary to reach more conclusive results.

Magnesium also crystallizes on a hexagonal close-packed lattice, although its resistivity is less anisotropic than that of cadmium. Several investigators have used magnesium alloys and the agreement among them, for instance, for the deviation in

Mg-Ag,[17,19] *Mg*-Cd,[17,19] and *Mg*-Al[19] (cf. Fig. 8), leads one to conclude that the texture of the specimens is the same in these different laboratories. It is particularly interesting that values of $\rho_i(273.2)$ determined for magnesium specimens in some of these laboratories and shown in Table IV agree with one another reasonably well but differ from the value 3.94 $\mu\Omega$ cm, to be expected for randomly oriented crystallites. If the specimen texture changes with impurity content, then it may readily be shown that there is a correction to be applied to Δ that may be of either sign but would require substantial changes of the crystallite alignment to account for the observed deviations. Further, since Δ is observed to be proportional to the solute concentration over a large temperature range in these alloys, the effect of texture could only invalidate our earlier conclusions if it varied in the same way. To test this hypothesis we attempted some x-ray determinations of crystallite orientation in the *Mg*-Al specimens. The construction of pole figures[37] for these fine wires is such an involved problem that it was decided instead to take Laue backreflection photographs of spark-cut and heavily etched cross sections of the wires. The pure magnesium specimens each showed evidence of some preferred alignment of the crystallites, but all photgraphs of the alloys showed that the crystallite orientation possessed circular symmetry with respect to the incident x-ray beam, which on one occasion was perpendicular to the wire axis. From the x-ray evidence we conclude that effects due to crystallite orientation will be nearly the same in each alloy and therefore cannot account for the observed deviations in the magnesium alloys.

CONCLUSIONS

Deviations from Matthiessen's rule have been obtained for 23 alloys from accurate resistivity measurements made between 1.5 and 300 °K on the alloys and several pure metal specimens. The observed deviations below about 40 °K are consistent with a contribution from inelastic scattering by impurities and one from a two-band mechanism. Above about 50 °K, a two-band contribution and an interference term between the inelastic scattering by impurities and by the phonon spectrum of the host lattice can account for the results in all except the *Cd*-Mg alloys, where different crystallite orientation in the pure and alloy specimens may have played a role. These experiments qualitatively confirm the predictions of Bhatia and Gupta regarding the temperature dependence of the deviations, particularly with respect to the difference in sign of $d\Delta/dT$ that occurs for the complementary alloy pairs: *Al*-Mg and *Mg*-Al; *Ag*-Cd and *Cd*-Ag; *Ag*-Mg and *Mg*-Ag; and *Al*-Ag and *Ag*-Al. Only when the interference term is included can the origin of negative deviations, which are often observed, be understood.

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Low-Temperature Specific Heat of Ruthenium

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Measurements of the specific heat of Ru have been performed in the temperature range 2–11.5 K. Values for the Sommerfeld γ and the Debye Θ of 3.10 ± 0.02 mJ/mole K^2 and 555 ± 6 K were obtained. Deviations of Θ from its limiting value were observed above 9 K. This value of Θ is in good agreement with the acoustically determined value, thus removing the discrepancy between calorimetric determinations of Θ and the acoustic results.

There is considerable disagreement on the values of the parameters which characterize the low-temperature heat capacity of Ru, the Sommerfeld γ, and the Debye Θ, between those experiments which allow determination of these parameters.[1–5] The existing situation is summarized in Table I and discussed briefly below. This study, the measurement of the heat capacity of Ru between 2 and 11.5 K, was prompted by the disagreement between the acoustically determined value of Θ[5] and that obtained in the analysis of the calorimetric data of Clusius and Piesbergen.[2] The Clusius and Piesbergen data seemed consistent with the acoustic data, provided that Θ increased slowly with decreasing temperature throughout the range 23–11 K rather than remaining constant below 23 K, as was assumed. If this is the case, a slightly larger value for γ than was obtained in the original analysis will be obtained. The results of this experiment were to find that this was the case. The limiting value of Θ was reached only below 9 K. The limiting value was in good agreement with the acoustic value. Little can be said of Wolcott's results,[1] which were obtained at temperatures as low as 1.2 K, since no results other than values of γ and Θ and the value of the heat capacity at 20 K were given. The values of γ ob-

TABLE I. The parameters which characterize the low-temperature heat capacity of Ru according to various experiments.

Calorimetric determinations	γ (mJ/mole K^2)	Θ(K)
Wolcott (Ref. 1)	3.35	600
Clusius and Piesbergen (Ref. 2)	2.6	505
This work	$3.10 \pm .02$	555 ± 6
Acoustic determinations		
Fisher and Dever (Ref. 5)		554
Critical field analysis		
Hulm and Goodman (Ref. 3)	1.2	
Finemore and Mapother (Ref. 4)	2.4	