Deviations from the Matthiessen Rule Due to Possible Changes in the Phonon Spectrum of Dilute Magnesium Alloys*

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The resistivity of polycrystalline alloys of magnesium with lithium, silver, cadmium or tin, in concentrations up to 1.3 at. % has been measured in the temperature range 1.2 to 300°K. The increase in resistivity at room temperature due to alloying (impurity resistivity) and the decrease in slope of the resistivity-temperature curve of the alloys with increasing alloy concentration, i.e., electron-per-atom ratio, agree with the results reported by Salkovitz, Schindler, and Kammer. An exception is the results for lithium, for which a smaller impurity resistivity has been found. The impurity resistivity may vary by as much as 10% from room temperature to the helium-temperature range. Below 20°K this temperature dependence satisfies the correction introduced by Kohler, which requires an increase in the impurity resistivity with respect to its value at 0°K, proportional to the ideal resistivity of the base metal. Instead of being a constant at higher temperatures, as the Kohler correction would imply, the impurity resistivity decreases for temperatures where the ideal resistivity exceeds the impurity resistivity. As a possible explanation it is suggested that the temperature-dependent part of the alloy resistivity is a corrected ideal resistivity of the pure metal. This leads then to a supposed decrease in the Debye temperature of the magnesium due to the presence of foreign atoms. This explanation and the order of magnitudes involved are in reasonable agreement with published data on the variation of the elastic constants of magnesium upon alloying. The results indicate that besides a change in the phonon spectrum the observed effects depend also on the electron-per-atom ratios for the alloys.

INTRODUCTION

PRELIMINARY results[1,2] of electric-resistance measurements with magnesium-neodymium alloys indicated interesting departures from Matthiessen's rule which could not immediately be connected with the properties of each of the components.

It seemed therefore of interest to investigate magnesium alloys with nonmagnetic (and better understood) metals as a second component. Alloys of this kind have been subjected to extensive crystallographic investigation before.

The classic x-ray measurements of the lattice spacings of dilute magensium alloys by Raynor[3] indicated an over-all contraction of the lattice for a number of solutes. Past a certain contraction and for elements having a greater valence than magnesium, the lattice expands in the direction of the hexagonal axis (c direction). Busk[4] has reported similar x-ray results with alloys of a chosen electron-per-atom ratio (e/a) for which expansion in the axis direction above the normal thermal expansion could be observed by raising the temperature.

These observations have been interpreted by Jones[5] as being a consequence of electrons occupying states in the second Brillouin zone in the direction of the hexagonal axis (B overlap). The calculations of Trlifaj[6] of

the electron energy spectrum in magnesium confirmed the overlap hypothesis. Based on pertinent experimental data on the Fermi surface the recent calculations by Falicov[7] indicate that a considerable overlap of electrons into the second and higher zones exists in the pure metal at the absolute zero. This theoretical result is in contradiction with the Jones explanation for the coupling between the onset of lattice expansion with an overlap. On the other hand, such a correlation is indicated by the x-ray and other experimental data. The present investigation will confirm this correlation in an indirect manner.

It was suggested by Salkovitz, Schindler, and Kammer[8] (further referred to as Salkovitz) that the overlapping electrons should affect the transport properties of polycrystalline alloys. Their measurements of the thermoelectric power at 78, 195, and 300°K and the Hall effect at 300°K with several solutes proved that this suggestion was correct. The solute concentrations at which discontinuities occur in these properties do not seem to be quite comparable to the x-ray results. It was also found that the impurity resistivity $\Delta\rho$, varies in general linearly with the solute concentration and is a function of solute valence rather than of size of the solute ion. In the temperature range $T = 293–308°K$, $d\rho/dT$ of the alloys was observed to decrease with increasing electron concentration. These results then indicate a departure from Matthiessen's rule for normal, nonmagnetic solutes in the room-temperature range. On the other hand, Hedgcock, Muir, and Wallingford[9] report that no devi-

[1] K. B. Das and A. N. Gerritsen, J. Appl. Phys. **33**, 3301 (1962).
[2] S. B. Das and A. N. Gerritsen, Phys. Rev. Letters **8**, 169 (1962).
[3] G. V. Raynor, Proc. Roy. Soc. (London) **A174**, 457 (1940), **A180**, 107 (1942).
[4] R. S. Busk, Trans. AIME **194**, 207 (1952).
[5] H. Jones, Proc. Roy. Soc. (London) **A144**, 235 (1934).
[6] M. Trlifaj, Czech. J. Phys. **1**, 110 (1952).

[7] L. M. Falicov, Phil. Trans. Roy. Soc. (London) **A255**, 55 (1962).
[8] E. I. Salkovitz, A. I. Schindler, and E. W. Kammer, Phys. Rev. **105**, 887 (1956).
[9] F. T. Hedgcock, W. B. Muir, and E. Wallingford, Can. J. Phys. **38**, 376 (1960).

TABLE I. Spectrographic analysis of the specimen.

Alloy	Al	Ca	Cu	Fe	Mn	Ni	Pb	Si	Sn	Zn	Sample indication (at. %)
					Weight percents						
Mg	<0.0001	<0.01	<0.0001	0.0010	0.0011	<0.0002	0.0005	<0.001	<0.001	<0.02	
0.16 Li	<0.001	<0.01	<0.001	<0.0005	<0.001	0.0009	<0.002	<0.005	<0.01	<0.001	0.56 Li
0.38 Li	<0.001	<0.01	<0.001	<0.0005	<0.001	0.0009	<0.002	<0.005	<0.01	<0.001	1.32 Li
2.45 Ag	<0.001	<0.01	<0.001	0.0012	<0.001	<0.001	<0.002	<0.01	<0.01	<0.001	0.56 Ag
5.30 Ag	<0.001	<0.01	<0.001	0.0029	<0.001	<0.001	<0.002	<0.01	<0.01	<0.001	1.25 Ag
3.12 Cd	<0.001	<0.01	<0.001	<0.0005	<0.001	<0.001	<0.002	<0.01	<0.01	<0.001	0.69 Cd
5.55 Cd	<0.001	<0.01	<0.001	<0.0005	<0.001	<0.001	<0.002	<0.01	<0.01	<0.001	1.25 Cd
0.047 Sn	<0.001	<0.01	<0.001	0.001	<0.001	<0.0003	<0.003	<0.001	<0.047	0.003	0.01 Sn
0.230 Sn	<0.001	<0.01	<0.001	<0.001	<0.001	0.0004	0.005	<0.001	0.230	0.003	0.05 Sn
0.65 Sn	<0.001	<0.01	<0.001	0.0005	<0.001	0.0007	0.010	<0.001	0.65	0.006	0.13 Sn
2.85 Sn	<0.001	<0.01	<0.001	0.0010	<0.001	0.0018	0.008	<0.001	2.85	0.004	0.60 Sn

ations from the Matthiessen's rule for a series of dilute magnesium alloys are observed in the range 2–35°K, except in the case of transition-element solutes.

For a two-band metallic conductor, assuming the ratio of ideal and residual resistances to be different in the two bands, Sondheimer and Wilson[10] have calculated a correction to the Matthiessen's rule which is qualitatively in agreement with a later published, more general treatment by Kohler.[11] The results can be formulated as follows. Assume that the impurity resistivity $\Delta\rho(T)$ given by

$$\Delta\rho(T)=\rho_a(T)-\rho_m(T) \tag{1}$$

(in which $\rho_a(T)$ and $\rho_m(T)$ represent the measured resistivities of the alloys and of pure magnesium, respectively), can be split additively into a constant residual part $\Delta\rho_r$ and a temperature-dependent part $\Delta(T)$

$$\Delta\rho(T)=\Delta\rho_r+\Delta(T). \tag{2}$$

The latter can be expressed in terms of the ideal resistivity $\rho_i(T)$ and the residual resistivity $\rho_r=\rho_a(0)\approx\Delta\rho_r$ as

$$\Delta(T)=\beta\gamma\rho_i(T)\rho_r/[\beta\rho_r+\gamma\rho_i(T)], \tag{3}$$

where

$$\rho_i(T)=\rho_m(T)-\rho_m(0).$$

It follows that

$$\Delta(T)=\gamma\rho_i(T) \quad \text{for} \quad \gamma\rho_i(T)\ll\beta\rho_r, \tag{3a}$$

and

$$\Delta(T)=\beta\rho_r \quad \text{for} \quad \gamma\rho_i(T)\gg\beta\rho_r. \tag{3b}$$

β and γ can be expected to be small and may depend on the type and concentration of the impurity. So far no rigorous experimental proof of (3) has been given.

For the particular case of a dilute magnesium alloy having $\Delta\rho_{273}\approx0.1\ \rho_{m273}$ one would expect saturation (3b) at 77°K where $\rho_{i77}\approx0.1\ \rho_{i273}$. Even when the onset of saturation would require a larger $\rho_i/\Delta\rho$ ratio, one

would always find at room temperature $d\ \Delta\rho/dT\geq0$. A negative value for this slope is against the Kohler correction.

A correction to Matthiessen's rule of much smaller magnitude is that arising from the higher order approximation to the conductivity. This correction has been calculated by Sondheimer[12] for a one-band, free-electron model. It turns out to be zero at 0°K and at high temperatures, but reaches a maximum in the temperature range where the ideal resistivity is of the same order as the residual resistivity. The magnitude of the correction is larger for the more impure material, even then for a sample with $\rho_r\approx0.3\ \rho_{i273}$ it amounts to only about 0.54% of the total resistivity. The small value of this correction and its rather fast decrease for temperatures above the maximum make it seem rather improbable that this would lead to the observation of $d\rho/dT$ values at room temperature that are smaller for the alloys than for magnesium.

It is the purpose of this paper to investigate the apparent contradiction between the observed obedience to Matthiessen's rule at low temperature and the deviation found in the room-temperature region, by determining the resistivity of magnesium and some alloys between 1.2°K and room temperature. In order to investigate a possible influence of the electron-per-atom ratio (e/a), two monovalent metals (lithium and silver) a bivalent metal (cadmium) and a tetravalent metal (tin) have been used as solutes.

EXPERIMENTAL PROCEDURE

The specimen of pure magnesium and the alloys were supplied by the Dow Metal Products Company, Midland, Michigan, in strips $15\times1.5\times0.015$ cm.[13] In Table I the pertinent spectrographic analyses of the various samples is given.

For the resistivity measurements at room tempera-

[10] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) A190, 435 (1947).
[11] M. Kohler, Z. Physik 126, 495 (1949).

[12] E. H. Sondheimer, Proc. Roy. Soc. (London) A203, 75 (1950).
[13] At a loss in the precision of the determination of resistivity this sample thickness was chosen in order to have reasonable low temperature resistance values while maintaining equal machining history for all samples, including the pure magnesium samples.

ture, samples were cut about 10 cm long and 5 to 8 mm wide. For the low-temperature measurements, a sample width of only 1 to 2 mm was chosen. After cutting, the samples were annealed in helium atmosphere at 330°C for 2 h to obtain minimum resistivity. The further preparation of the samples and the room-temperature resistivity measurements have been described earlier.[1]

The low-temperature measurements in the ranges 1.3–4.2°K, 14–20°K, and 78°K were carried out with the sample in contact with the bath. For the ranges 78–273°K, the sample was enclosed in a double-walled brass chamber, with a conventional heating arrangement. During a measurement, the sample chamber was filled with helium exchange gas, and heated above the bath temperature. A thermal leak to the liquid bath was controlled by adjusting the vacuum between the chamber walls. Pure annealed No. 36 commercial copper wire, calibrated against a standard platinum resistance thermometer was used to measure the temperature in the sample chamber in the range 78–273°K.

In order to check the reproducibility of the copper wire thermometer, three different lengths of the same spool of wire were mounted with normal precautions to avoid stress and kinks. For these three lengths, the average temperature coefficient of resistance $(R_{273}-R_{90})/(183\times R_{273})$ was determined to be $(4.404 \pm 0.004)\times 10^{-3}$ degree^{-1}. Using this value and the measured resistance of the wires, a maximal spread of $\pm 0.02°$K in the calculated range of temperature was found between the wires. This is a remarkably good result for a simple thermometer.

The samples and the copper thermometer were electrically in series with a regulated power supply (Lambda LA 50-03B or LT 2095). The voltages were measured with a 5-dial Diesselhorst compensator (manufacturer Bleeker) and a Zc-Kipp galvanometer as zero instrument (sensitivity better than 10^{-7} V/unit deflection).

RESULTS

The Resistivity Increase at 273°K

The resistivity of the pure magnesium used was determined to be 4.17 ± 0.02 $\mu\Omega$cm at 273°K. This is in good agreement with the value 4.18 $\mu\Omega$cm reported by Das and Gerritsen[1] for Johnson-Matthey material, but rather large compared with the value 4.119 $\mu\Omega$cm for Dow material as reported by Salkovitz. In terms of the resistance ratio $r'_{4.2}=R_{4.2}/R_{300}$, the purity of the magnesium seems to be rather high, when compared with similar ratios reported in various recent papers (see Table II).

The impurity resistivity $\Delta\rho$ is calculated from the alloy resistivity ρ_a and the measured resistivity of the magnesium ρ_m according to (1).

Figure 1 shows the variation of $\Delta\rho_{273}$ with the concentration c of the Li, Ag, Cd, and Sn solutes. The proportional change of $\Delta\rho$ with c is qualitatively in agreement with the results obtained by Salkovitz which are in-

TABLE II. Resistance ratio $r'_{4.2}$ for pure magnesium.

Author	Stock	$10^3 r_{4.2}$	
Stark et al.[a]	Dow Chem.	2.2	Single crystal
Alekseevskii et al.[b]		1.6–4.3	Single crystal
Present authors	Dow Chem.	1.3; 1.7	Polycrystalline
Hedgcock et al.[c]	Dow Chem.	3.6	Polycrystalline
Yntema[d]	Johnson Matthey Lab. No. 1848	4.7	Polycrystalline

[a] R. W. Stark, T. G. Eck, and W. L. Gordon, Phys. Rev. **133**, A443 (1964).
[b] N. E. Alekseevskiĭ and Yu. P. Gaĭdukou, Zh. Eksperim. i Teor. Fiz. **38**, 1720 (1960) [English transl.: Soviet Phys.—JETP **11**, 1242 (1960)].
[c] See Ref. 9.
[d] G. B. Yntema, Phys. Rev. **91**, 1388 (1952).

cluded in the figure. With the thin samples used our precision in the resistivity measurements is at best $\pm\frac{1}{2}\%$, which results in a general spread of the order of ± 0.05 $\mu\Omega$cm in the $\Delta\rho_{273}$ values. Considering this, the agreement between both results is remarkably good. However, the smaller resistivity increase reported in this work for the Mg-Li alloys is beyond the range of experimental error. The present results yield the value $\Delta\rho_{273}/c = 0.45$ $\mu\Omega$cm/at.% against 0.755 $\mu\Omega$cm/at.% as given by Salkovitz. The values $\Delta\rho_{273}$, $\Delta\rho_{78}$ and $\Delta\rho_{4.2}$ are tabulated in Table III together with the corresponding r-values $(r=R_T/R_{273})$ for the alloys investigated.

TABLE III. Impurity resistivity $\Delta\rho$ and relative alloy resistance r at three temperatures for different alloys.

Alloy	$\Delta\rho_{273}$ $\mu\Omega$ cm	r_{78}	$\Delta\rho_{78}$ $\mu\Omega$ cm	$r_{4.2}$	$\Delta\rho_{4.2}$ $\mu\Omega$ cm
Mg	···	0.1291	···	0.0017	···
0.56 Ag	0.368	0.2093	0.406	0.0845	0.372
1.25 Ag	0.745	0.2499	0.761	0.1282	0.710
0.56 Li	0.211	0.1937	0.316	0.0655	0.280
1.32 Li	0.649	0.2554	0.700	0.1244	0.593
0.69 Cd	0.322	0.2227	0.431	0.0886	0.391
1.25 Cd	0.836	0.2965	0.915	0.1691	0.840
0.01 Sn	0.064	0.1409	0.035	0.0144	0.054
0.05 Sn	0.221	0.1845	0.249	0.0610	0.261
0.13 Sn	0.659	0.2717	0.771	0.1562	0.748
0.60 Sn	1.986	0.4157	2.018	0.3175	1.949

Results Below 20°K

The pure magnesium samples exhibit a minimum in the resistivity around 4°K, with a rise of about 3% at 1.3°K. Since the sample resistivity at 4°K is 7×10^{-3} $\mu\Omega$cm, this effect of the minimum is negligible with respect to $\Delta\rho_r$ values encountered. The ideal resistivity is therefore conveniently computed as $\rho_i(T)=\rho_m(T)-\rho_m(4.2)$. Also, as no temperature dependence is observed in the alloy resistivity below 4°K, ρ_r is taken to be $\rho_a(4.2)$, or $\Delta\rho_r=\Delta\rho_{4.2}$.

In Fig. 2 the values $\Delta\rho_T$ as computed with (1), are plotted against T for the alloys in the range 1.3 to 20°K. The number at each curve is the value $\Delta\rho_r=\Delta\rho_{4.2}$ in 10^{-9} Ωcm; the scale is for all cases equal to the double arrow indicating 6×10^{-9} Ωcm. In general, there is a
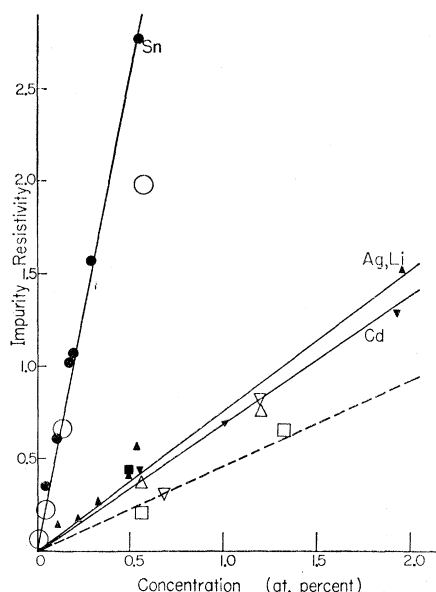
FIG. 1. Concentration dependence of the impurity resistivity at 273°K. Index: Ag (▲△), Li (■□), Cd (▼▽), and Sn (●○). Solid symbols and lines represent the results reported by Salkovitz et al. (Ref. 8). The dashed line as suggested by the present results for Mg Li.

monotonic rise in the impurity resistivity above 4°K. For a comparison of this rise with (3), a set of curves $\Delta\rho(T) = \Delta\rho_r + \gamma\rho_i(T)$ is also included in the figure. Using (3a) for the measured values at 20°K, γ was found to be in the range 0.7 to 1.0 in most cases. However, with values of $\gamma = 0.8$ for the more dilute alloys with $\Delta\rho_r < 0.4$ $\mu\Omega$cm and $\gamma = 1.0$ for the more concentrated alloys, a fairly good agreement with the experimental data is observed.

In Fig. 2 are two cases that at first sight do not seem to follow the general pattern. In the case of the 1.32 Li alloy a small rise in the $\Delta\rho_r$ is suggested by the results in the range 14–20°K. This may be the result of incidental cold work since this sample needed remounting between the measurements in the liquid helium and the hydrogen resulting in an addition of 2×10^{-9} Ωcm in $\Delta\rho_r$. As for the 0.01 Sn alloy the result can clearly not be described with $\gamma = 0.8$; a value $\gamma = 0.5$ would be better. On the other hand, the requirement for the applicability of (3a) may not be satisfied for this alloy, ρ_r is comparable to ρ_i within this range of temperature.

The correspondence between $\Delta(T)$ and $\rho_i(T)$, which itself is proportional to a high power of T in the considered range of temperatures is a rather convincing proof that the change in $\Delta\rho$ is caused by temperature scattering. It also suggests that the mechanism of the deviation as proposed by Kohler[11] is acceptable.

Results Above 20°K

Above 20°K, $\Delta\rho$ values are plotted in Fig. 3, representing $\Delta\rho(T)$ for temperatures up to 293°K. The verti-

cal lines at each measured point indicate the spread in the value, which will be discussed later. Contrary to (3b), Δ (which is the difference between the inserted values and $\Delta\rho$) does not approach saturation. After passing through a maximum Δ decreases monotonically. This decrease may lead at higher temperatures to $\Delta\rho$ values lower than the residual resistivity $\Delta\rho_r$. The negative slopes in the $\Delta\rho(T)$ curves around 273°K agree qualitatively (Fig. 4) with the decrease with respect to pure magnesium of the temperature dependence of the resistivity as reported by Salkovitz.

The ideal resistivity at the temperature of the maximum is found to be comparable to the residual resistivity for the alloy, satisfying the relation $\rho_i(T_{max}) = x\rho_r$, where x is found to be a constant for a given solute. This is shown graphically in Fig. 5 where the values $x\rho_r$ plotted against the temperature of the maximum for each alloy, lie fairly well along the $\rho_i(T)$ curve for magnesium. The values of x used for the different solutes, Ag, Li, Cd and Sn, are 1.5, 1.5, 1.0, and 0.33, respectively.

DISCUSSION

The present results indicate an impurity resistivity increase at 273°K in Mg-Cd and Mg-Ag alloys that tends to be lower than those reported by Salkovitz,
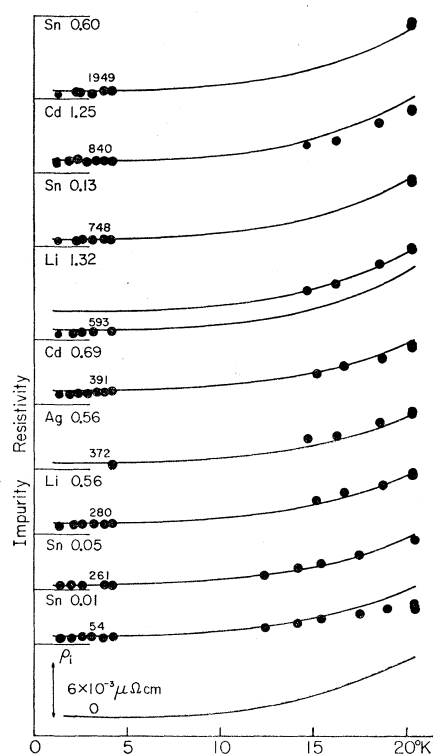

FIG. 2. The temperature dependence of the impurity resistivity below 20°K as compared with the calculated Kohler correction (full lines). The vertical scale is for each sample as indicated by the double arrow for the ideal resistivity curve. The numbers above the lines are the values of the impurity resistivity $\Delta\rho_r$ in nano ohm cm at 4°K.
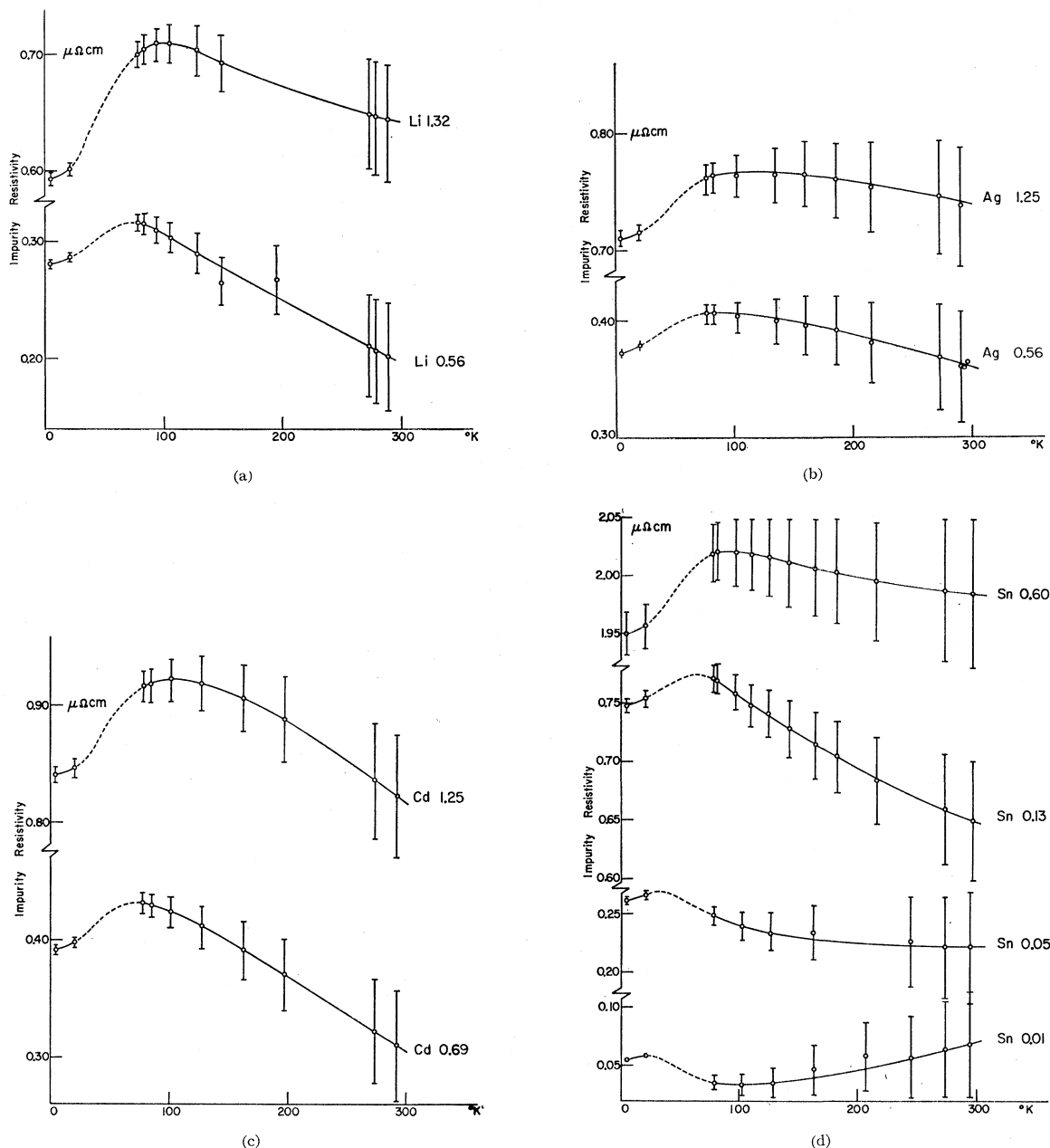
Fig. 3. The temperature dependence of the impurity resistivity below 300°K. 3a. Mg-Li; 3b. Mg-Ag; 3c. Mg-Cd; 3d. Mg-Sn. The vertical lines indicate the average deviation in the determination of ρ_a at 273°K.

though the difference is not large enough to suggest a disagreement. The results for Mg-Sn agree very well, up to the concentration where a change of slope in the $\Delta\rho(c)$ curve is evident. However, as stated earlier, there is a marked difference in the $\Delta\rho/c$-value for Mg-Li: 0.45 $\mu\Omega$cm/at.% as against 0.775 $\mu\Omega$cm/at.% reported in their paper. That the atomic resistivity increase $(\Delta\rho/c)$ should depend only on e/a as suggested by Salkovitz, is rather unexpected since it would eliminate the effect of other properties on $\Delta\rho/c$. In this respect, the mono-

valent metals Li and Ag are not equivalent, the solubility of Li in Mg being an order of magnitude larger. It has been pointed out [14] that apart from reasons such as the more favorable size factor, the similarity in the general characteristics of the ions of Li and Mg due to their diagonal positions in the first two periods of the periodic table enables Li to be packed with greater ease in the Mg lattice. One could therefore expect Li to cause

[14] G. V. Raynor, *The Physical Metallurgy of Magnesium and its Alloys* (Pergamon Press, New York, 1959), Chap. 5, p. 119.
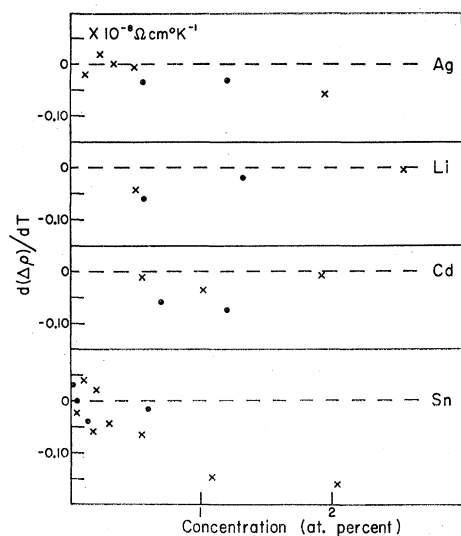
FIG. 4. Comparison between the present values of $d(\Delta\rho)/dT$ (dots) and those reported by Salkovitz et al. (crosses, Ref. 8).

a smaller change in resistivity as compared to Ag, when alloyed with Mg.

The discussion of the results on the temperature dependence of resistivity requires a consideration of the precision of the measurements. It is clear that any discussion of changes in resistivity depends strongly on the precision limited by geometrical errors with which ρ is determined at room temperature, since the precision in the determination $r(T)$ a resistance *ratio*, is better by orders of magnitude. In a recent discussion of the Kohler deviation in Al, Sn, and Cu alloys, precisely these difficulties were considered by Alley and Serin.[15] They correctly point out that since the magnitude δ_ρ of the error in ρ varies with temperature, e.g. $\delta_\rho(T) = r(T)\delta_{\rho273}$, this may lead to an erroneous interpretation of temperature effects in $\Delta\rho$. In order to avoid these difficulties, they assume that $\Delta\rho$ is constant between 198 and 348°K, and thus arrive at suitable values for $\Delta\rho$ at 273°K from the measured resistance ratios $r(T)$ for the alloys and for the pure base metals. The fact that this could be done for all their specimens enabled them to fix an upper limit[16] for the increase of $\Delta\rho$ with temperature, while a decrease in $\Delta\rho(T)$, with increasing temperature was entirely discounted by theoretical considerations as being unreasonable.

It is very difficult to use such an assumption in the present case, considering that the decrease in $d\rho/dt$ of an alloy with increasing e/a ratio, as reported by Salkovitz, cannot easily be connected to a geometrical error which is more or less constant for different samples. Therefore, the room-temperature resistivity of each sample is reported as the arithmetic mean of values obtained for

different sections along the sample length. An average spread of $\pm0.5\%$ which includes the spread in the geometrical measurements is estimated in the room temperature resistivity. Since this is a sample error, a spread amounting to $\pm1\%$ in $\rho_a(T)$ is expected to be found in the corresponding $\Delta\rho_T$. This spread is indicated by the vertical lines in Fig. 3, the lines being reduced by the factor r_T at temperature T. Below 20°K, where the variation of r is such that the error can be considered to be constant, the absolute value of $\Delta\rho_T$ may be affected but not its temperature dependence. The variation of Δ at low temperatures as ρ_i is therefore to be accepted within these considerations. Within the rather conservatively chosen range of the spread of the data, the temperature dependence of Δ at higher temperatures seems to be unambiguous for some alloys. It is obvious that the results for the Mg-Ag alloys would not easily justify any other than the conclusion that Δ is a constant within the experimental precision, even when the smaller rms errors were indicated. With the support of the data obtained with the other alloys, the conclusion that Δ decreases fits in the general pattern and will be justified later. In the perusal of these curves, it should be noted that an actual spread in the data is observed only for the low-concentration alloys where $\Delta\rho$ is small in magnitude.

The existence of the relation between ρ_r and T_{max} (Fig. 5) is difficult to explain in terms of errors in the determination of $\Delta\rho$. Consider the condition (3b) for the saturation of Δ, in connection with this. From (3b) it follows that for saturation to occur at temperature T, $\rho_i(T) = y\beta\rho_r/\gamma$, where $y\gg1$. Taking the value of β to be $\beta' = \Delta(T_{max})/\rho_r$, it is found that $y = x\gamma/\beta'$ varies from 8 to 18 for all the alloys. It is therefore reasonable to assume that the saturation in $\Delta\rho$, under the condition given by Kohler sets in near T_{max}, and that in first approximation, the value of Δ at T_{max} gives the level of saturation. It then follows that $\beta = \beta'$ has the values 0.085, 0.16, 0.10, and 0.04 for the alloys with Ag, Li, Cd, and Sn, respectively. This agrees in order of magnitude with the values 0.05, 0.08, and 0.11 for the Cu, Sn, and Al base alloys,[15] the difference being, however, that for magnesium alloys the parameter depends on the nature of the solute.
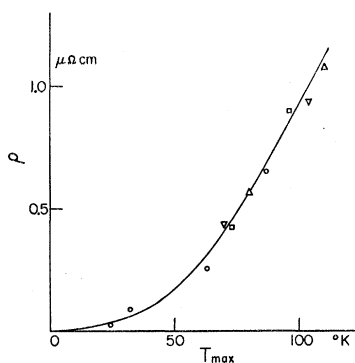
[15] P. Alley and B. Serin, Phys. Rev. **116**, 334 (1959).
[16] A. N. Gerritsen and J. M. L. C. Van der Aa, Appl. Sci. Res. **A6**, 191 (1956).

FIG. 5. Values $x\rho_r$ (□ Li, △ Ag, ▽ Cd, ○ Sn plotted against T_{max} for each alloy. The curve represents the ideal resistivity.

Except for the decrease in $\Delta\rho$ to $\Delta\rho_r$ that follows from the Sondheimer calculations,[10] there is no physical evidence so far to support a decrease in $\Delta\rho$ with further increase in temperature. Application of these calculations to the case of a magnesium alloy with $\Delta\rho_r \approx 0.8$ $\mu\Omega$cm shows that the maximum correction, equal to 1% of $\Delta\rho_r$, is expected around 95°K. Only in the case of the 1.20 Ag alloy is the decrease in $\Delta\rho$ for $T>T_{max}$, though of the order a few percent, comparable to this predicted decrease, whereas for the 1.20 Cd and 0.13 Sn alloys the decrease in $\Delta\rho$ is an order of magnitude larger and even overcompensates the total Kohler correction. For dilute alloys of 0.6 Au in Ag and 1.0 Ag in Au, Krantz and Schultz[17] report Kohler corrections with $\gamma \approx 1.3$ and $\beta \approx 0.08$, β corresponding to a constant $\Delta \approx 0.08\Delta\rho_r$ for $T>150$°K. They claim that a maximum of approximately 0.02 $\Delta\rho_r$ in the $\Delta(T)$ curve for both samples is evidence of the Sondheimer correction. This conclusion has been criticized by Alley and Serin.[15]

The correlation of T_{max} with the ideal resistivity, that is with the scattering of the electrons by the phonons, suggests that the observed decrease in $\Delta\rho$ for $T>T_{max}$ might be correlated with a correction to be applied to ρ_i. Assuming then that the smaller values of $\Delta\rho$ can be attributed to values of ρ_i that are too large one can define a corrected ρ_i^* for the phonon scattering in the alloys as

$$\rho_i(T)-\rho_i^*(T)=\Delta\rho^*(T)-\Delta\rho(T) \quad \text{for} \quad T>T_{max},$$

and

$$\rho_i(T)=\rho_i^*(T) \quad \text{for} \quad T<T_{max}.$$

Taking $\Delta\rho^*(T)=\Delta\rho(T_{max})=$ constant then the Kohler correction (3)

$$\Delta(T)=\beta\gamma\rho_i^*(T)/(\beta\rho_r+\gamma\rho_i^*(T)) \qquad (4)$$

holds for all temperatures, with ρ_r the residual resistivity as measured.

For $T>T_{max}$, the fraction

$$f(T)=\frac{\Delta\rho(T_{max})-\Delta\rho(T)}{\rho_i(T)}=\frac{\rho_i(T)-\rho_i^*(T)}{\rho_i(T)} \qquad (5)$$

represents an estimate of the fractional change in $\rho_i(T)$. It is found that f is positive and changes differently with temperature and with concentration for the various types of impurities. As an illustration the f values for an arbitrarily chosen temperature $T=2.5 \ T_{max}$ are listed in Table IV.

It is possible to interpret the correction to be applied to ρ_i in terms of an effective Debye temperature θ of the alloy. For a given metal, the ratio of the resistivity at low temperatures (ρ_1, for $T_1 \ll \theta$) and that at high temperatures (ρ_2, for $T_2 \gg \theta$) can be written as[18]

$$\frac{\rho_1(T_1)}{\rho_2(T_2)}=\text{const}\left(\frac{T_1}{\theta}\right)^4\frac{T_1}{T_2}. \qquad (6)$$

TABLE IV. Fractional decrease in the phonon resistivity f of the alloy with respect to pure magnesium (at $T=2.5T_{max}$) and the difference δ in c spacing between the alloy and pure magnesium.

Alloy	T_{max} °K	$10^2 f(2.5 T_{max})$	δ X units
0.56 Li	73	2.2	− 0.3
1.32 Li	96	1.3	− 6
0.56 Ag	80	0.7	− 5
1.25 Ag	110	0.5	−14
0.69 Cd	70	2.0	− 2
1.25 Cd	104	2.0	− 4
0.01 Sn	24	2.8	(− 0.04)
0.05 Sn	32	3.7	− 0.2
0.13 Sn	63	2.8	− 0.5
0.60 Sn	87	0.7	+ 1

For $T_2 > T_{max}$ the results indicate that $\rho_i^*(T_2) < \rho_i(T_2)$, and for $T_1 < T_{max}$ it is assumed that $\rho_i^*(T_1)=\rho_i(T_1)$. Hence

$$\rho_i^*(T_1)/\rho_i^*(T_2) > \rho_i(T_1)/\rho_i(T_2),$$

and with (6) it follows that $\theta^* < \theta$. For the alloys considered, the decrease in θ would be less than 1%. The application of (6) is of course a crude procedure. Firstly, with measurements made only up to temperatures which are at most 0.8θ, the condition $T_2 \gg \theta$ is not satisfied. Secondly, there is no proof that $\rho_i^*(T_1)=\rho_i(T_1)$ below T_{max}, though the smallness of ρ_i suggests changes in the phonon spectrum to be beyond observation. However, other experiments confirm the possibility of a decrease in θ. The room-temperature values of the elastic constants of dilute alloys of Mg-Ag, Mg-In and Mg-Sn have been reported by Long and Smith.[19] The measurements have been repeated and extended to 78 and 4.2°K by Eros and Smith.[20] It is generally observed that the elastic constants decrease as the e/a is increased from 2.000 to 2.020. Below $e/a=2.000$ however, Long and Smith[19] report a tendency of the elastic constants to increase from lower values to those of Mg, while the latter authors observe a decrease of the constants when e/a changes from 1.995–2.000. The maximum change in the elastic constants is of the order of 2%, and the ratios relative to the values for pure Mg have a temperature dependence of $\sim 0.1\%$. From general considerations[21] then, the variation of the elastic constants with solute concentration suggests a decreasing Debye temperature for tri- and tetra-valent solutes. This is confirmed by the specific heat measurements of Rayne[22] on dilute Mg-Al alloys, where a decreasing value for θ is reported up to additions of 2 at.%Al. For monovalent solutes, the results are not unambiguous; but on the basis of the better accuracy claimed by Eros and Smith[20] one would expect θ to increase for additions of silver.

It is obvious that the changes in the elastic constants

[17] E. Krantz and H. Schultz, Z. Naturforsch. 12A, 710 (1957).
[18] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1958), 2nd ed., Chap. 9, p. 279.

[19] T. R. Long and C. S. Smith, Acta Met. 5, 200 (1957).
[20] S. Eros and C. S. Smith, Acta Met. 9, 14 (1961).
[21] L. J. Slutsky and C. W. Garland, Phys. Rev. 107, 972 (1957).
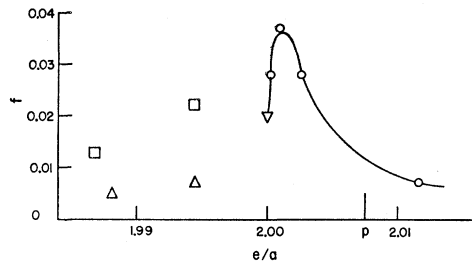[22] J. Rayne, Phys. Chem. Solids, 7, 268 (1958).

FIG. 6. The relative change f in the ideal resistivity plotted against the electron/atom ratio for the different alloys ($\square$ Li, $\triangle$ Ag, $\triangledown$ Cd, $\circ$ Sn).

are mutually correlated with changes in θ and e/a. The low precision in f allows only for an attempt to separate qualitatively the lattice and electronic effects.

In Fig. 6 the f values (taken arbitrarily for $T = 2.5T_{max}$ in order to made a comparison possible) are plotted against the e/a values for the alloys investigated. For both Cd alloys $f = 0.02$, this then represents the effect for an alloy in which e/a equals the magnesium value. With decreasing or increasing e/a, f changes accordingly. The value $e/a = 2.075$, indicated by p on the abscissa, is the value for which the x-ray indicates that the decrease in the c parameter changes into an increase. This seems to be coupled with the decrease in f.

Now f represents the decrease in the resistivity due to phonon interaction. Up to $e/a = 2.075$ the c parameters of all alloys considered decrease with increasing amounts of the solutes[23] (Table IV). In this qualitative approach the relatively small decrease in the a parameter of the crystal is not considered. For all alloys then the change in c and θ results in an increase in the number of low-energy phonons and a corresponding decrease in the number of high-energy phonons. The increase is in a temperature region where the phonon scattering is already low, and will be incorporated in the low-temperature rise of the resistivity described in

[23] See Ref. 14, Table 16, p. 98.

terms of the Kohler correction. The decrease in the number of the high energy phonons is observed as the decrease in resistivity. This effect then can be partially annihilated by an accompanying decrease in e/a (Li, Ag) or enhanced by an increase in e/a (Sn). The reversal of the change in c adds again phonons of higher energy and consequently the resistivity increases. If one were to extrapolate the data for the Li and Ag solutes to the line $e/a = 2.00$, the number f so obtained would correspond to the true lattice effects for these alloys. Considering that the change in the lattice parameter c is per atomic percent two to three times larger for silver than for other alloys, one may ask whether the distribution of the values f on $e/a = 2.00$ is related to the phonon distribution curve at the Debye cutoff.

CONCLUSIONS

The present results confirm for a number of magnesium alloys the temperature dependence of the additive impurity resistivity at low temperatures as suggested by Kohler (1949). The validity of this approach can be extended to higher temperatures by essentially replacing the undisturbed lattice of pure magnesium by one that is disturbed because of the presence of impurities. The corresponding decrease in the Debye characteristic temperature does not seem to be in contradiction with specific-heat measurements and some observed changes in the elastic constants of magnesium upon alloying. The effect seems to be the result of a combination of changes in particular in the lattice c-spacing and in the electron distribution.

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