Phonon resistivity in Mg-Yb alloys

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The temperature-dependent part of the electrical resistivity of polycrystalline pure magnesium and Mg-Yb alloys with different concentrations have been measured from 4.2 to 300 K. The phonon resistivity of the pure Mg and Mg-Yb alloys varies as T^n, where $2.5 < n < 5$–6. At intermediate temperatures the deviation from the Matthiessen's rule (DMR) passes through a small maximum. The temperature corresponding to the maxima of DMR shifts to higher values with the impurity concentration as $\sim c^{1/5}$. At high enough temperatures the sign of the derivative $\rho_0^{-1} d\Delta(T,c)/dT$ is positive.

I. INTRODUCTION

The investigation of the deviation from Matthiessen's rule (DMR) is very important for understanding the various transport properties of metals. The main physical reasons leading to the DMR generally are the following[1]: (a) inelastic scattering (inelastic phonon and inelastic impurity scattering); (b) anisotropic scattering (two bands, anisotropic phonon spectrum, anisotropic impurity scattering, anisotropic Fermi surface, thermal umklapp scattering, electronic distribution anisotropy); (c) resonant scattering; (d) miscellaneous (change in phonon spectrum, phonon-impurity interference, electron-electron scattering, loss of translation symmetry, phonon drag).

Until now the temperature-dependent part of the electrical resistivity of pure magnesium and magnesium-based alloys has not been investigated very thoroughly and only few results in limited ranges of temperature have been reported,[2-4] although the deviation from Matthiessen's rule of Mg alloys have been explored by many investigators.[2,3,5,6] In particular the DMR for the magnesium-containing rare-earth solutes have been investigated by Das *et al.*[7] (Mg-Gd) and by Hedgcock *et al.*[8] (Mg-Ce). In the Mg-Gd alloys of higher concentration only a small DMR were found, while the measurements on Mg-Ce alloys have shown smaller or no DMR.

On the other hand, Mg is like the noble metals in that the presence of very small quantities of certain rare-earth-metal impurities lead to the appearance of a Kondo minimum in the electrical resistivity. The Mg-Yb system shows such a minimum between 1.6 and 4.2 K.[9]

Since magnesium-containing solutes of elements from the beginning (Ce) and the middle (Gd) of the 4*f* period show small or no DMR, it is of interest to study the DMR of Mg-containing impurities at the end of the 4*f* period (Yb) in order to show whether all rare-earth impurities in Mg cause any DMR.

Also we have made precise measurements of the temperature-dependent part of the electrical resitivity of the pure Mg and of the Mg-Yb alloys in order to clarify the scattering processes which can take place in Mg and its alloys.

II. EXPERIMENTAL PROCEDURE

The samples (supplied by Battele's Columbus Laboratories, Ohio) used in this investigation were polycrystalline pure magnesium (99.95%) with a residual resistivity ratio about 900 and magnesium alloyed with 0.021-, 0.084, 0.47-, and 1.16-at.% ytterbium (99.9%). The melting of the alloys was performed in a small clay-graphite crucible heated by gas flame, with salt fluxes used to protect the molten metal from oxidation. The initial slabs were rolled into foils about 100 μm thick. From these foils the sample shapes were stamped out with a special steel press tool. The samples were rectangular (20×2 mm^2) with two similar extensions for voltage contacts. Since the DMR depends very sensitively on the specimen geometry, one requires very precise measurements of the dimensions of the samples and particularly of the thickness. The geometry factor of the samples was determined by a conventional microscope with an accuracy of about $\pm 0.2\%$. After the stamping out, and in order to obtain a final homogenization, the samples were annealed for 10 h at 450 °C in a helium-gas atmosphere. The Yb concentration was determined by chemical analysis, while the impurity contents in pure Mg and Mg-Yb alloys were analyzed spectroscopically.

The experimental measurements were carried out in a standard stainless-steel cryostat containing liquid helium or liquid nitrogen. The temperature can be controlled by a heater coil wrapped around a 100-mm-long copper tube which surrounds the sample holder. The sample holder consists of anodic oxidated aluminum plates between

which the samples can be sandwiched. The intimate thermal contact between the highly conducting sample holder and the samples reduces thermal gradients and allows the use of a larger sample current for the resistivity measurements without Joule heating effects. The temperature was determined by three calibrated copper-Constantan thermocouples mounted directly in the sample holder. During each measurement the temperature was determined always better than ±0.5 K. The measurements were performed between 4.2 and 300 K.

The sample voltage was first amplified by a photoelectric galvanometer amplifier (Amplispot Sefram, France) and then displayed on a Dana digital voltmeter, while the current source maintained a current constant to 10^{-5} over short periods of time. Elimination of stray emf's was achieved by reversing the current direction. The data were then transferred to an on-line desk calculator (Hewlett-Packard 9821 A) to give the average values. The relative accuracy of the measurements was about 10^{-4} and the resolution ±5 nV.

III. RESULTS

The measurements of the residual resistivity ρ_0^a of alloys at 4.2 K show that there is not a linear relationship between ρ_0^a and the Yb concentration. This means that the Yb atoms are not randomly distributed in the Mg matrix but form clusters. Optical microscope investigations show that the Mg–0.084-at.% Yb alloy exhibits very finely distributed precipitations within the grains, while the Mg–0.47-at. % Yb alloy shows two different precipitation types, namely large gray precipitations within the grains and fine precipitations at the grain boundaries. Probably, the eutectic begins here. The Mg–1.16-at.% Yb alloy shows ternary eutectic precipitations at the grain boundaries and finely distributed precipitations within the grain.

In Fig. 1 the deviations from Matthiessen's rule $\Delta(T, c)$ for the Mg-Yb alloys are plotted as a function of the temperature. The deviation $\Delta(T, c)$ is defined as

$$\Delta(T, c) = [\rho_a(T) - \rho_p(T)] - (\rho_a^0 - \rho_p^0) , \quad (1)$$

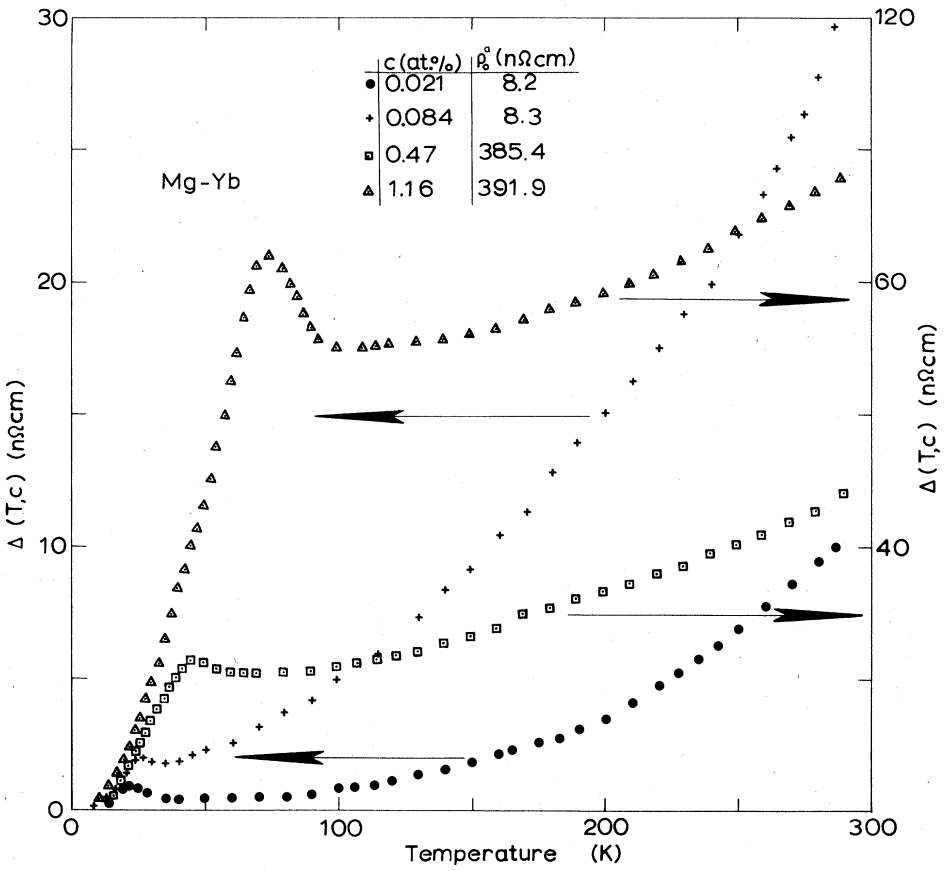

FIG. 1. Temperature dependence of the deviation from Matthiessen's rule in Mg-Yb alloys.

where $\rho_a(T)$, $\rho_p(T)$ are the measured resistivities, and ρ_a^0, ρ_p^0 the residual for the alloyed and pure samples, respectively.

In order to obtain $\Delta(T, c)$, it is necessary to know the residual resistivity of the alloys ρ_a^0 in the presence of a Kondo minimum. The impurity resistivity $\rho_a(T)$ of the Mg-Yb alloys[9] increases approximately logarithmically as the temperature is lowered. The calculated values of the residual resistivities ρ_a^0 and hence $\Delta(T, c)$ were obtained above 4.2 K by fitting the temperature data of the resistivities (between 1.6 and 4.2 K to the Kondo formula[10]

$$\rho_{\text{Kondo}} = \rho_m[1 + 2J_{sf}(g-1)\mathfrak{N}(\epsilon_F)\ln T] \quad . \tag{2}$$

In the formula (2), ρ_m is the de Gennes factor[11] given by

$$\rho_m = \frac{\pi m \mathfrak{N}(\epsilon_F)}{e^2\hbar n}\, c(g-1)^2 j(j+1) J_{sf}^2 \quad , \tag{3}$$

where c is the concentration of Yb ions, n is the number of conduction electrons per unit volume, $g_{Yb^{3+}} = \frac{8}{7}$ the Lande factor, $\mathfrak{N}(\epsilon_F)$ (= 0.28 $\text{eV}^{-1}\,\text{atom}^{-1}\,\text{spin}^{-1}$) is the density of states of Mg at ϵ_F and J_{sf} was taken as $J_{sf} = 0.11$ eV. The calculated values of the resistivities above 4.2 K were extrapolated to $T = 0$ K and so the final values of ρ_a^0 were obtained.

The principal features of the deviations $\Delta(T, c)$ are: (i) positive deviation at low temperatures, (ii) a flat maximum (called "hump") at intermediate temperatures, which shifts with the Yb concentration and becomes more and more pronounced with increasing the Yb contents, and (iii) in the high-temperature region the deviations $\Delta(T, c)$ are nearly linear in T and show positive slopes.

In Fig. 2 the behavior of the quantity $[\rho(T) - \rho_0^{\text{ext}}]/T^3$ instead of $\Delta(T, c)$ is shown for pure Mg and its Yb-alloys together with previously pure-Mg measurements[2-4].

$[\rho(T) - \rho_0^{\text{ext}}]/T^3$ is plotted as a function of the temperature in a log-log plot, where $\rho(T)$ is the measured resistivity at the temperature T. From this figure it can be seen that the phonon resistivity $\rho(T) - \rho_0^{\text{ext}}$ of the pure Mg as well as of the Mg-Yb alloys cannot be characterized by a single power law. In the temperature region 4.2–7 K the phonon resistivity of the pure Mg varies between T^5 and T^6. As the temperature increases the phonon resistivity goes over to a T^3 plateau, and between 12 and 20 K $\rho(T) - \rho_0^{\text{ext}}$ varies as $T^{2.5}$. At the temperature 20 K the phonon part of the resistivity of the pure Mg goes through a minimum and then increases as $T^{3.4}$ until 50 K. Between 50 and 70 K $\rho(T) - \rho_0^{\text{ext}}$ varies again with T^3, and in the temperature region 70–150 K there is a T^2 behavior of $\rho(T) - \rho_0^{\text{ext}}$. Above 150 K the variation of $\rho(T) - \rho_0^{\text{ext}}$ is proportional to T.

The present measurements of pure Mg are in good agreement with those of Notley *et al.*[4] [the residual resistivity ratio (RRR)~1500], where there is a discrepancy at low temperatures with the measurements of Seth and Woods[3] (RRR~700) and Hedgcock and Muir[2] (RRR~400), respectively. Recently, Alderson and Hurd[12] measured the tem-

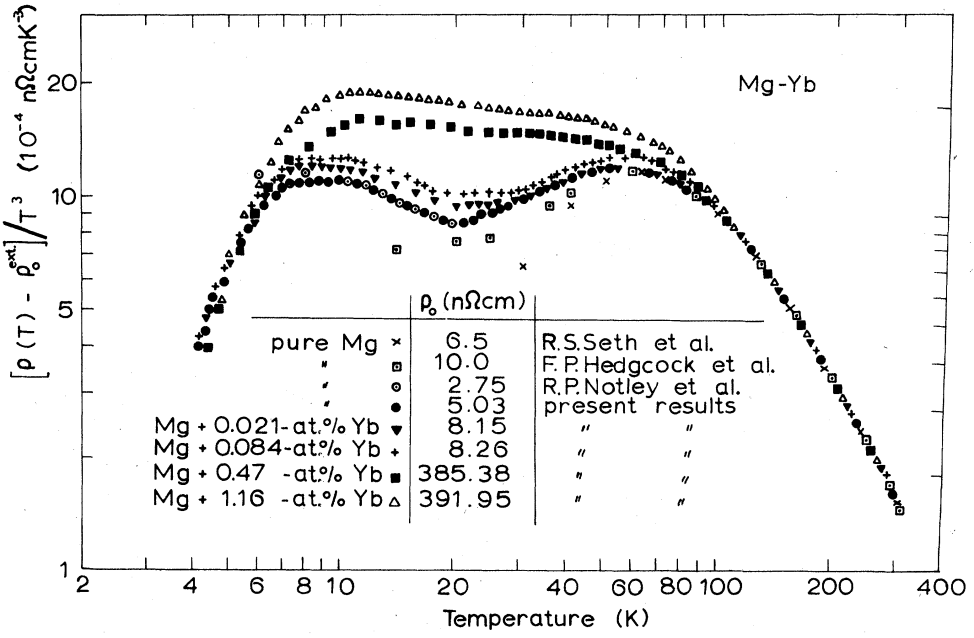

FIG. 2. Temperature and impurity dependence of the quantity $\rho(T) - \rho_0^{\text{ext}}/T^3$.

perature-dependent part of the resistivity of pure monocrystals of Mg (RRR~420), and they found that $\rho(T)$ has a $T^{3\cdot3-3\cdot4}$ dependence between 6 and 50 K.

The same temperature dependence of the phonon resistivity is also exhibited by the two alloys with the lowest Yb contents. On the other hand, when the Yb concentration increases, although the temperature dependence of $\rho(T)-\rho_0^{ext}$ remains the same below 6 K, in the temperature region 10–50 K the "double-maximum" structure of the phonon resistivity disappears and $\rho(T)-\rho_0^{ext}$ varies approximately as T^3. At the lowest temperature (< 6 K) the phonon resistivity is independent of the impurity concentration.

Figure 3 shows the temperature-dependent part of the resistivity $\rho(T)-\rho_0^a$ of Mg-Yb system as a function of the residual resistivity ρ_0^a in a semilogarithmic plot for five different fixed temperatures. These isotherms include also the previous published data on other Mg-alloyed systems, which are taken from Cimberle *et al.*[13] From this figure it can be seen that the data points are widely spread, which can be attributed to experimental problems, such as the metallurgical condition of the alloys, the high residual resistivity of the pure Mg, anomalous resistivity variation (Kondo effect), etc.

Despite the experimental difficulties, the general pattern of the present and previous data does suggest a constant $\rho(T)-\rho_0^a$ at low ρ_0^a values and an increase at higher ρ_0^a values. The constant values of $\rho(T)-\rho_0^a$ indicate a possible value of the so-called "dilute" or "pure" limit. Because the data are too scattered it is difficult to extract any significant parameters.

IV. DISCUSSION

Unfortunately, until now there has not been any detailed calculation on the temperature-dependent part of the resistivity of the pure polycrystalline hcp metals and, in particular, of magnesium. The only calculation is that of Borchi *et al.*,[14] who have calculated the electron-phonon part of the resistivity of the pure polycrystalline hcp metals using the Ziman-Baym theory[15,16] and the harmonic theory of lattice dynamics in the one-phonon approximation with the assumption

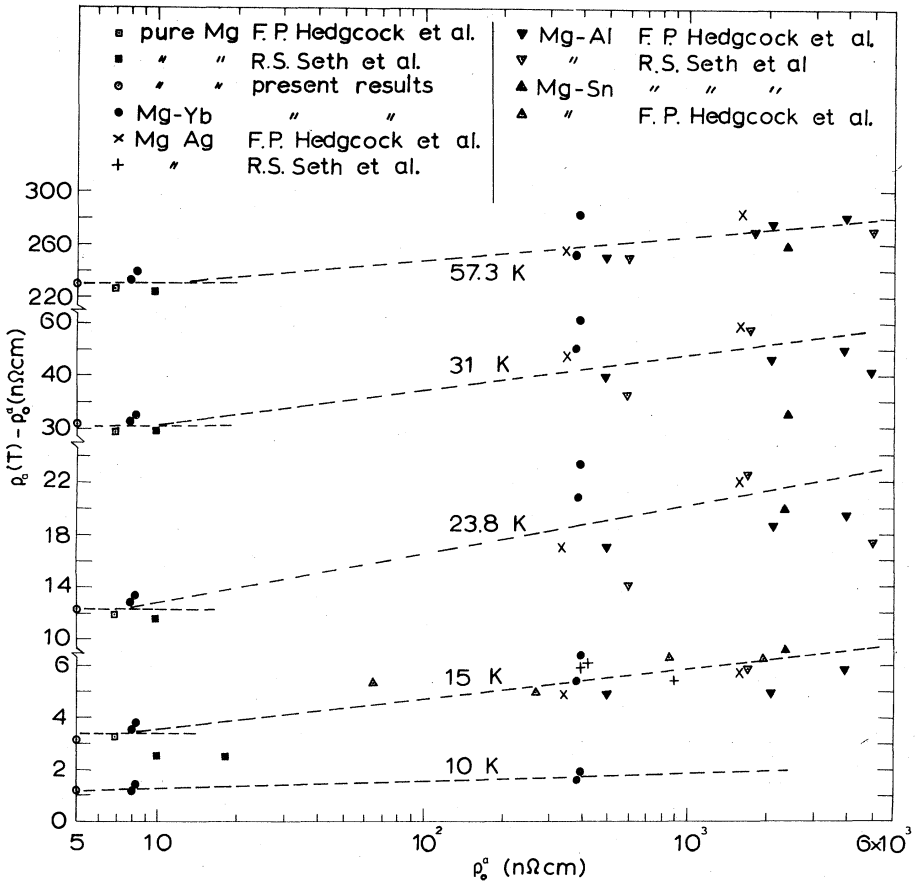

FIG. 3. $\rho(T)-\rho_0^a$ as a function of the residual resistivity ρ_0^a at five representative temperatures.

that the phonons are in thermal equilibrium.

If one takes into account that the umklapp processes are dominant, the Borchi *et al.*[14] calculation gives a T^2 term for the resistivity at low temperatures. This result is in disagreement with the present experimental results of pure polycrystalline Mg, which shows a T^n dependence with $6-5 < n < 2.5$ in the temperature region 4.2–70 K. The discrepancy between the experimental data and theoretical calculation can be attributed to the failure of the one orthogonalized-plane-wave approximation of the theoretical model.

On the other hand, the phonon part of the resistivity of the Mg-Yb alloys with the highest concentrations is very similar to Lawrence and Wilkins[17] calculation. They have calculated the temperature dependence of the resistivity of polyvalent metals (Al and Zn) in the "dirty limit" due to electron-phonon umklapp processes, which are expected to be important at low temperatures. Lawrence and Wilkins[17] found that below some characteristic temperature Θ_1, which is of the order $0.01-0.05\Theta_D$ (Θ_D is the Debye temperature, for Mg $\Theta_D = 320$ K), umklapp processes contribute to the phonon resistivity as T^5 but with a coefficient which is greater than that for the resistivity due to the phonon normal processes. For temperatures above Θ_1 the phonon resistivity due to umklapp processes cannot be characterized by a single-power law and is given by two leading terms with temperature dependence T^2 and T^4, respectively. These two predictions are in agreement with the present experimental results. Namely, there is a T^{5-6} temperature dependence of the resistivity up to about $0.02\Theta_D$ and above this temperature the phonon resistivity cannot be described by a single power law.

The most characteristic feature of these measurements is that the DMR, in contradiction to the previous experiments on Mg–rare-earth alloys,[7,8] passes through a pronounced maximum called "hump". This hump shifts with the Yb concentration. In Fig. 4 the temperature T_{max} corresponding to the maximum of $\Delta(T)$ is plotted against the Yb concentration in a double logarithmic diagram. It can be seen that T_{max} shows the same behavior as the Al alloys,[18–20] i.e., T_{max} varies as $\sim c^{1/5}$, except for the Mg–1.16-at.% Yb alloy. This departure can be attributed only to the metallurgical condition of these alloys, as mentioned above.

The existence of the humps in DMR and the shift of their position with concentration as $\sim c^{1/5}$ for the intermediate temperatures observed in the present investigation, makes it possible to carry out a direct comparison with the theory of Kagan and Zhernov.[21] According to Kagan and Zhernov[21] this effect is attributed to the change in the anisotropy of the electronic distribution function. This anisotropy arises as a result of both anisotropic phonon spectrum and thermal umklapp processes in electron-phonon interaction. The introduction of impurity atoms suppresses the anisotropy of the distribution function due to the elastic scattering on impurities. The isotropization of the distribution function begins to play an important role at the intermediate-temperature region in the temperature-dependent part of the resistivity and this leads to a nonlinear dependence of $\rho(T)$ on the impurity concentration c for small values of c.

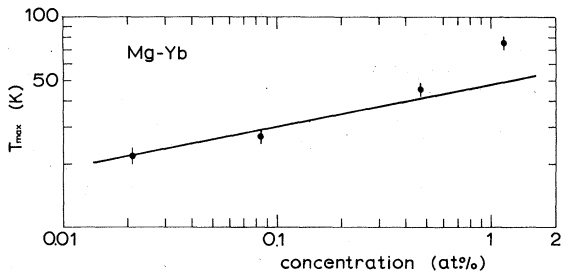

FIG. 4. T_{max} against solute concentration.

We shall now confine our discussion to the DMR, at high-temperature region. There are two different model calculations, which provide the framework for a possible explanation of the DMR in this temperature range. Kagan and Zhernov[21,22] attributed linear components in $\rho(T, c)$ to interference between scattering of electrons from phonons and from impurities. They asserted that the sign of the derivative $\rho_0^{-1} d\Delta(T, c)/dT$ would usually be the same as the sign of the difference between the ionic charges of the impurity and the host ion in the host lattice.

On the other hand, Bhatia and Gupta[23] predict that the interference term leads to a linear dependence of $\Delta(T, c)$ on T and that the slope $\rho_0^{-1} d\Delta(T, c)/dT$ should change sign when the solvent and solute atoms are interchanged.

The present experimental results are in agreement with Kagan and Zhernov[21,22] if one assumes that the valence of the Yb impurities is trivalent in Mg as in the low temperatures.[9] This assumption, on the other hand, is in contradiction with the x-ray parametric investigations, which predict the divalent nature of ytterbium in these alloys.[24]

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