# Resistivity of polycrystalline dilute magnesium, rare-earth alloys between 4.2 and 373 K and the application of the Friedel theory

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The resistivities of a number of polycrystalline Mg samples containing less than 0.1 atomic percent of each of the rare-earth metals Ce through Lu (with the exception of Pm) have been measured for 4.2 K, 77 K, and in the range 193 to 373 K. The resistivity per atomic percent of solute was determined from the relation between alloy resistivity and the solute concentration, and varies between 0.58 and  $8.9 \,\mu\Omega$  cm/at. % at 4.2 K. The results indicate that the contribution of the direct exchange to the electron scattering is small (on the order of 0.4 eV), whereas that of the Coulomb screening is an order of magnitude greater. A periodicity is found in the plot of the resistivity increase against the atomic number of the solute. This is in general agreement with Friedel's theory for the case of virtual bound, nondegenerate 4*f* bands that pass through the Fermi level of the solvent with increasing atomic number of the solute. The results indicate the presence of a virtual bound state generated by Gd, Tb, and Dy solutes. A valence instability for Ce ions is probably observed. The resistivity increase for Eu is found to be extremely small, on the order of 0.15  $\mu\Omega$  cm/at. %.

### INTRODUCTION

About 40 years ago Linde<sup>1</sup> reported the results of a systematic investigation of the room-temperature resistivity of elements dissolved in the noble metals. A result of this work was that the impurity resistivities for iron-group solutes showed large deviations from Norbury's rule that the impurity resistivity of solute elements in a solvent should increase proportional to the square of the difference between the atomic numbers of solute and solvent. The observed behavior of the iron-group solutes was explained by Friedel<sup>2</sup> by considering the screening of the extra charge in the 3d states leading to the concept of virtual bound states. This concept has been worked out for rare-earth (R) solutes as well,<sup>3</sup> but has so far not been confirmed by experiment.

The model can be briefly described as follows. An impurity with a number of electrons  $(\Delta Z)$ different from that for the host metal will cause Coulomb screening by the conduction electrons of the base metal at the impurity site. With progressing  $\Delta Z = 1, 2, 3, \ldots$  the screening potential will increase and the corresponding energy state will move downward from above the Fermi level into the conduction band. These states are named virtual bound states (VBS), with d and f character for the transition and R metals, respectively. Their half-width is large ( $\approx 1 \text{ eV}$ ) for the iron-group transition metals and small ( $\approx 0.02$ eV) for the R metals as an impurity. Under certain conditions the spin degeneracy of the d and f states can be dissolved. The difference in energy for the two opposite-spin configurations is of the order 0.6 eV, and only when this is greater than  $1/\Delta Z$  times the width of the VBS a split in

spin-up and spin-down states will occur. The width of the VBS is determined by the crystal potentials in the base metal and is, therefore, different for different base metals. With the center of the VBS at  $E_F$  the lifetime of a conduction electron in the VBS will be largest ("resonance scattering") and the resistance increase due to the addition of the iron-group impurities will pass for an unsplit state through a maximum at Mn. Such is the case for an Al solvent. In the case of a Cu base, the splitting of the 3d states will give rise to two passages through  $E_F$  and consequently two peaks in the resistance  $\Delta Z$  plot are observed around Fe and Ti. This qualitative approach and the argumentation leading to the results has been modified and placed in a quantitative frame by others<sup>4</sup> and its importance has been discussed by several authors.5-7

In the case of R impurities for which the width of the VBS is 0.02 eV, the condition for a split of the 4f level is satisfied for  $\Delta Z > 0.3$  and one can, in the appropriate base metal, expect resistance peaks at  $\Delta Z = 3\frac{1}{2}$  and  $10\frac{1}{2}$ , that is between Pm and Sm and between Ho and Er. Furthermore, because of the small width, one can expect temperature-dependent scattering when the temperature is 200 K or higher. Magnesium was chosen as a solvent for different reasons. Important was the intuitive argument that interaction between solute f states and a solvent d might state add a new complication.

## EXPERIMENTAL PART

Several problems in the investigation have been brought to an acceptable solution, but not without leaving some uncertainty in the results. The low solubility<sup>8</sup> of the R elements in Mg causes the

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formation of inclusions of the phase  $Mg_{1-x} R_x$ , with in general  $x \approx 0.1$ . The molten alloy mixture was, therefore, quenched and the solid ingot annealed at a temperature above the eutectic line ( $\approx 590^{\circ}$ C). A scanning electron microscope (SEM) was used to find the intensity distribution of the appropriate *L*-fluorescence line of the *R* solute. The method of preparation resulted in an overall homogeniety with variations up to 20% in certain spots.

The large anisotropy in the electrical conduction of Mg is probably the reason that the resistivity of pure Mg samples, prepared from the same batch (sublimated Mg, Dow Chemical) differed from sample to sample. For eight samples the averaged resistivity at 273 K was  $\rho_{p}(273) = (3.978)$  $\pm$  0.147)  $\mu\Omega$  cm, or  $\pm$  3.7% spread. The resistance ratio at 4.2 K,  $\rho(273)/\rho(4.2) = 1614 \pm 37.1$ , so that  $\rho_{b}(4.2) = (0.0025 \pm 0.00015) \ \mu\Omega \text{ cm}.$  These spreads are much larger than the 0.01% and (the better than) 0.1% precision in the determinations of the resistance and the form factor of the samples (diameter ~3 mm, length  $1\frac{1}{2}$  to 3 cm). It is obvious that small, solute-generated resistivity increases ( $\approx 0.1 \ \mu\Omega$  cm) can only with reliability be determined as the difference between the alloy resistivity ( $\rho_a$ ) and  $\rho_b$  from the data taken at 4.2 K. Therefore, the atomic resistivity increase  $\delta \rho(T)$  was determined for each temperature as the slope of plots of  $\rho_a$  against the concentration c of the solute. In most cases though, the spread in the high-temperature values of  $\delta \rho$  computed by the two different methods was much less that the spread in  $\rho_b$  values would suggest. This could be due to a smaller anisotropy effect with impurities present.

The solute concentration in each sample was determined in the Van de Graaff linear accelerator in this laboratory by a method described elsewhere.<sup>9</sup> The precision in c is of the order 1 to 2%. Impurities besides the R, in particular R other than the desired one, were sometimes found in magnitudes less than 1% of the concentration of the introduced solute.

# **RESISTIVITY RESULT**

For the 4.2-K data and in a few cases for the 77-K data as well, a nonlinear variation for  $c \leq 0.02$  at % was observed. Unless stated otherwise this smaller initial slope was in general ignored. Data for  $\delta\rho(T)$  for the different *R* solutes are listed in Table I.

Two exceptional cases should be discussed. For  $c \leq 0.03$  at. % Ce  $\delta\rho(T)$  is much larger than it is above this concentration: For T = 273 K the values are 5.67 (c < 0.03 at. %) and 1.46  $\mu\Omega$  cm, respectively, the latter compared to  $\approx 1.6 \ \mu\Omega$  cm

at. % reported in the literature<sup>10</sup> for c > 0.03at. %. Phase inclusions above 0.03 at. % (though not observed with the SEM) could cause such an effect. But Ce exhibits in its metallic state pressure-dependent phase changes,<sup>11</sup> and its single 4f electron is assumed<sup>12</sup> to be very loosely bound. These observations may well be connected and could lead for atoms in solution to a concentration-dependent change in their atomic configuration.

The MgEu samples were consistently checked for inclusions; the solute distribution was not different from that for the other alloys. Nevertheless the observed  $\delta \rho$  values are extremely low.

## **COMPARISON WITH THEORY**

The scattering of the conduction electrons with impurity ions with incomplete d or f shells is composed of two parts. Electrons (holes) in these levels require neutralization by the conduction electrons. This gives rise to Coulomb screening potentials that hinder the motion of the conduction electrons. Secondly, the conduction electrons, through their magnetic moment interact with the net magnetic moment of the impurity ion. The total effect of this Coulomb and direct exchange on the atomic resistivity increase can be written<sup>13</sup> in the form

$$\Delta \rho = \alpha \left[ A^2(0) + (G-1)^2 J (J+1) K^2(0) \right] \tag{1}$$

with

$$\alpha = \frac{3}{2}m^* N_i / hE_F N_h^2 e^2 \,. \tag{2}$$

The Coulomb and direct interaction integrals are represented, respectively, by  $A^2(0)$  and  $K^2(0)$ ,  $N_i/N_h$  is the fraction of R atoms in the host with  $N_h$  atoms per m<sup>3</sup>,  $E_F$  is the Fermi energy of the host in eV, and  $\Delta \rho$  is the resistivity increase in  $\Omega$ m. J is the total angular quantum number of the impurity ion. G is the Landé factor and

$$G = 1 + [J(J+1) + S(S+1) - L(L+1)]/2J(J+1), \qquad (3)$$

with the ionic spin and orbital quantum numbers S and L. A plot of  $\delta\rho$  (4.2) against  $(G-1)^2 J(J+1)$ , for a series of impurities in the same base metal, can give information of the partial contribution of each of the two scattering contributions. Figure 1 is such a plot for  $\delta\rho(4.2)$ ; the values for L, S, and J have been taken from the literature.<sup>14</sup> At first sight one might conclude that the present case of R in Mg, (2) is only partially satisfied for Gd, Tb, and Sm only. However, ignoring the  $\pm 10\%$  possible error bars, the dotted lines indicate groups for which the direct exchange (slope of the lines) is approximately equal, but differ in the contribution by the Coulomb interaction. Pr and Yb are separate, and the high  $\delta\rho$  value

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Element	$\delta \rho$ in $\mu \Omega$ cm/at. %					$\delta \rho(T) / \delta \rho(4.2)$	
	4.2 K	77 K	193 K	273 K	373 K	77 K	373 K
Ce <sup>a</sup>	0.58	0.70	1.10	1.46	1.87		
Ce <sup>b</sup>	6,38	7.70	3.77	5.67	6.81	1.20	1.07
Ce <sup>c</sup>				(1.66)			
$\mathbf{Pr}$	3.70	3.77	3.22	2.95	2.72	1.02	0.74
Nd	7.81	7.94	7.23	6.59	5.97	1.02	0.76
Nd <sup>d</sup>		(9.5)		(9.5)			
Sm	8.14	7.86	8.14	8.01	7.95	0.97	0.98
Eu	0.18	0.22	0.72 <sup>e</sup>	е	е		
Gd	8,90	9.13	9.21	8.67	8.17	1.03	0.97
Gd <sup>d</sup>		(8,2)		(8.2)			
$\mathbf{Tb}$	8.60	8.82	7.73	7.48	7.14	1.03	0.83
Dy	7.77	7.67	5.59	4.30	2.76	0.99	0.36
Ho	6.53	$7.81^{f}$	6.97	6.90	6.84	1.20	1.04
Hog	(8.56)						
Er	8.50	9.14	8.99	7.73	6.25	1.07	0.74
Er <sup>g</sup>	(8.90)						
Tm	7.50	7.51	4.69	3.37	1.83	1.00	0.24
Yb	3.91	3.80	3.01	2.68	2.22	0.97	0.56
Lu	6.18	6,92	8.49	9.83	11.64	1.12	1.88

TABLE I. Values for the atomic resistivity increase and their ratios between 4.2 K and 77 K and 373 K, respectively. Overall precision is of the order of 10%. Values in brackets have been reported in the literature.

<sup>a</sup> For c > 0.04 at.%.

<sup>b</sup>Initial slope.

<sup>c</sup>Reference 10.

<sup>d</sup>J. Bijvoet, B. de Hon, J. A. Dekker, and G. W. Rathenau, Solid State Commun. <u>1</u>, 237

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 $^{e}\delta \rho(T) < 0$  for small c.

f Two alloys only.

<sup>g</sup> J. Bijvoet, G. Merlyn, and P. Frings, J. Physica B86-88, 535 (1977). Estimated values.

for Ce combines with Ho and Lu. The numerical values for the slopes of the three lines that follow from the data are, from top to bottom, 0.068, 0.081, and 0.078, respectively. With the first value it follows that  $K(0) = 0.29 (m_0/m^*)^{1/2}$  eV, and from the intercept at 7.90  $\mu\Omega$  cm/at. %, A(0) = 3.09 $(m_0/m^*)^{1/2}$  eV. In the computation the value  $E_F = 7.11$  eV has been used for the Fermi energy for Mg. Since<sup>15</sup>  $0.1 \le m^*/m_0 \le 1.45$ , a choice of an average value 0.5 for this ratio yields K(0) $\approx 0.4$  eV and  $A(0) \approx 4.4$  eV. It has been suggested<sup>16</sup> that a relatively small effect of the direct-exchange interaction can be expected in this case. Direct-exchange energies for Gd, Tb, Dy, Ho, and Er dissolved in Lu have been reported<sup>17</sup>: K(0) = 48 eV and A(0) = 0.89 eV. For R elements in Y positive and negative values of the same order of magnitude as those listed here have been observed.<sup>18</sup> The Coulomb scattering is, so far, indeed found to be the main contribution to the total scattering. Comparing this contribution for the case of Mg with those for R solved in heavier elements, 19, 20 one finds that A(0) is largest for a light and "true" s-p scattering metal such as Mg and that indeed, notwithstanding the problems in-



FIG. 1.  $\delta\rho(4.2)$  against  $(G-1)^2J(J+1)$  for a rare earth dissolved in Mg to illustrate the direct and indirect exchange effects. The bars represent a highest possible 10% error.

volved with its use as a solvent, it is the better choice to investigate the variation of the Coulomb scattering with the different R solutes. Added to this is the consideration that the d bands of heavier solvents are often situated close to or at the Fermi level. The atomic resistivity increase due to Coulomb scattering can be written in its simplest form for each of the two halves of the 4f shell as

$$\delta \rho \propto \sin^2(f \pi \Delta Z/7) \,. \tag{4}$$

 $\Delta Z = 1, 2, 3, \dots 7$  is the number of electrons in the 4f shell when moving from Ce...Gd and from Tb...Lu. The factor  $f \leq 1$  accounts for the possibility of broken values for  $\Delta Z$ .

The result from curve matching of (4) is given in Fig. 2 in which  $\delta\rho(4.2)$  has been plotted against  $\Delta Z$ . A correction should be applied for the directexchange scattering. The only cases where the magnitude thereof is significant is for the elements Gd, Tb, and Dy. One finds the following representations: Curve 1,  $\delta\rho(4.2) = 8.82 \sin^2$  $(0.83\pi\Delta Z/7)$  fitted through Nd and Sm; curve 3,  $\delta\rho(4.2) = 8.56 \times \sin^2(0.95\pi\Delta Z/7)$  fitted through Er and Yb. Ce, Eu, Gd, Tb, Dy, and Lu are not on the curves so constructed. Apart from the data for Gd, Tb, and Dy solutes one could claim that the Friedel theory describes the variation of the resistivity increase for R solutes in Mg, with a split 4f VBS



FIG. 2. The resistivity increase at 4.2 K for the rareearth solutes. Curves 1 and 3 are curves [Eq. (4)] for split 4f states, matched through data at the peak. Curve 2 is that for an unsplit 4f state, matched through for direct-exchange-corrected data (triangles). The bars represent a possible 10% error.

as the source of the periodicity. An unsplit VBS cannot account for the results as shown by the dashed curve in Fig. 2, constructed through the direct-exchange corrected values for Gd and Dy. For these elements dissolved in Ag or Au, the existence of an unsplit 5d VBS has been suggested.<sup>22</sup> Such a curve can just as well be constructed through the three values under discussion, but that would not prove anything either.

More information can, in principle, be obtained by considering the temperature dependence of  $\delta\rho$ . In Fig. 3, are plotted the values for the ratios  $\delta\rho(77)/\delta\rho(4.2)$  (triangles) and  $\delta\rho(373)/\delta\rho(4.2)$ (circles) from Table I against the  $\Delta Z$  of the solutes. The first ratio is practically constant  $(1 \pm 0.2)$  over the whole range, but the second one shows a periodicity with minima at positions close to the peaks in Fig. 2. The points for Gd, Tb, and Dy will shift somewhat downward when the values are corrected for the direct exchange.

The position of a VBS with respect to the Fermi level and its movement from one R to the next is accounted for, in particular, in the changes in the values of the ratio  $\delta\rho(373)/\delta\rho(4.2)$ . Remembering that the width of the VBS is of the order 0.02 eV and that 373 K corresponds to  $\sim 0.03$  eV, it follows that this ratio is less than 1 for resonance. When the VBS is outside the 0.03-eV limit, the ratio equals 1 when the (mostly small) common deviations from the Matthiessen rule are ignored. The ratio can be greater than 1 when the VBS is within the 0.03-eV range but outside the energy of the conduction electrons at 4 K ( $\approx 0.4$  meV). A further complication, of course, is that in Mg hole conduction is important. Also, one has to construct these curves for more temperatures, in particular in the interval 77 to 373 K for more precise data before any pertinent conclusion about the shift of the VBS with increasing  $\Delta Z$  can be made.



FIG. 3.  $\delta\rho(373)/\delta\rho(4.2)$  (circles and  $\delta\rho(77)/\delta\rho(4.2)$  (triangles) for the different rare-earth solutes.

#### CONCLUSIONS

The atomic resistivity increase of the R elements dissolved in Mg varies with their atomic number in a manner that suggests an agreement with the Friedel theory in its simplest form. But it is also found that possibly other states than only the split 4f states are involved in the scattering process. The direct spin exchange is small and seems to be of the same magnitude for all elements. The observed temperature-dependent atomic resistivity increase may eventually be correlated with the relative position of the virtual bound state of a particular R with respect to the Fermi level of the host.

*Note added.* A more detailed report on this investigation is available from Purdue University, Department of Physics, Solid State Office, West Lafayette, IN 47907; ask for Magnesium-rareearth Report.

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