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ELECTRICAL RESISTIVITY OF RARE-EARTH ALLOYS*

F. A. Smidt, Jr.[†] and A. H. Daane

Institute for Atomic Research and Department of Chemistry

Iowa State University, Ames, Iowa

Abstract—Resistivities of solid solution alloys in the systems Gd-Lu, Tb-Lu, Gd-Er, and Y-Lu were measured from 4.2-320°K to determine the behavior of the resistivity in alloy systems with magnetic phenomena arising from localized magnetic moments. A large contribution to the residual resistivity is caused by the random distribution of these localized moments through the lattice. An analysis of the lattice resistivity of the metals shows large variations across the heavy rare-earth series which are possibly correlated with the change of c/a ratio of the metals and the attendant changes in the Fermi surface geometry.

INTRODUCTION

One of the most sensitive and yet one of the most complex physical properties of metals and alloys is their electrical resistivity. It is known to be dependent upon the electronic structure, elastic constants and magnetic interactions but the nature of this dependence is not completely understood, particularly in the case of the transition metals. Scandium, yttrium, and the rare-earth metals, which might be considered as the

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[†]Present address: Hanford Atomic Works, Richland, Washington.

first members of the transition series by virtue of their incomplete d shells, have the same number of conduction electrons, similar elastic constants, atomic sizes, and crystal structures and thus provide excellent subjects for a study of the resistivity behavior in transition metals.

Magnetic phenomena in the rare-earth metals probably arise from an exchange interaction between the unpaired 4f electrons localized on the ion core and the conduction electrons, hence the magnetic ordering has a profound effect on the resistivity.^(1,2) This study was undertaken to investigate the dependence of the resistivity on magnetic interactions in rare-earth solid solution alloys. Studies of the alloy systems Gd-Lu and Tb-Lu, where magnetic rare-earth metals were diluted by the weakly paramagnetic metal lutetium, demonstrated the differences between magnetism arising from localized electrons and the collective electron type found in Ni-Pd alloys,⁽³⁾ and confirmed the prediction of Mott and Stevens⁽⁴⁾ concerning the resistivity behavior of alloys with magnetism arising from localized electrons.

To provide a more meaningful comparison among members of the rare-earth group, the magnetic contribution to the resistivity was subtracted from the total and the variations thus revealed were interpreted as differences in the Fermi surface configuration.

EXPERIMENTAL

The rare-earth metals used in the alloys were prepared by the method described by Spedding and Daane.⁽⁵⁾ The alloys were prepared by arc melting the constituents together under an argon atmosphere a sufficient

number of times to insure homogeneity. The alloys were obtained as rods by a "manometric" casting method in which the alloys were melted in vacuum and forced up into an inverted tantalum crucible by bleeding a small quantity of argon into the system. A radiographic method of inspection was used to detect the few castings with shrinkage cavities which were rejected. The castings were then machined into rods $3/8$ in. in diameter and 2 in. in length.

The resistivity was measured by the standard four probe method with current reversal. A cryostat and temperature controller described by Colvin, Legvold, and Spedding⁽⁶⁾ were used to attain the desired temperatures over the range 4.2-320°K.

Powder methods were used to obtain the x ray diffraction data and the lattice constants were determined by Cohen's method programmed for an I. B. M. 650 computer.

RESULTS

The existence of complete solid solubility in the systems Gd-Lu, Tb-Lu, and Gd-Er was confirmed by x ray diffraction and resistivity methods.

Plots of the cell volumes versus composition indicated that these solid solutions were very nearly ideal as would be expected from their similar properties. Plots of the c/a ratio versus composition for these alloy systems did not follow a linear relation but showed a minimum as shown in Table 1. This behavior is very similar to that observed across the heavy rare-earth series where the c/a ratio decreases from Gd to Er and then rises to Lu.

Table 1. X ray diffraction data

Sample	a(Å)	c(Å)	c/a	Vol. (Å ³)
Gd	3.639	5.789	1.5907	66.41
Tb	3.606	5.698	1.5804	64.15
Er	3.561	5.594	1.5707	61.44
Lu	3.506	5.555	1.5845	59.14
80.2 Gd-Lu	3.614	5.729	1.5851	64.82
57.3 Gd-Lu	3.589	5.681	1.5829	63.38
40.2 Gd-Lu	3.565	5.644	1.5832	62.11
20.0 Gd-Lu	3.539	5.604	1.5835	60.77
93.4 Tb-Lu	3.601	5.687	1.5793	63.85
66.7 Tb-Lu	3.583	5.655	1.5781	62.87
46.7 Tb-Lu	3.563	5.618	1.5771	61.75
23.3 Tb-Lu	3.537	5.587	1.5798	60.51
81.8 Gd-Er	3.626	5.753	1.5867	65.50
63.7 Gd-Er	3.615	5.719	1.5819	64.73
45.0 Gd-Er	3.601	5.686	1.5791	63.86
25.7 Gd-Er	3.587	5.650	1.5751	62.94

The temperature dependent portion of the resistivity versus temperature curves for the alloys is shown in Figs. 1-4. The sharp change in slope in the curves was interpreted as being due to the onset of magnetic ordering. The ordering temperatures given in Table 2 were determined from the discontinuity in plots of $\Delta\rho/\Delta T$ versus T for each of the alloys. These temperatures varied approximately linearly with composition.

The ρ versus composition curves are shown in Figs. 5-7 at 50° intervals. The isotherms for the residual resistivities evaluated at 4.2°K conform approximately to the parabolic behavior predicted by Nordheim's rule for solid solution alloys, although the maximum is displaced slightly due to the effects discussed in the succeeding section on electronic structure. The unsymmetrical shape of the curves at higher

Fig. 1. Resistivity versus temperature data for Gd-Lu alloys.

Fig. 2. Resistivity versus temperature data for Tb-Lu alloys.

Fig. 3. Resistivity versus temperature data for Gd-Er alloys.

Fig. 4. Resistivity versus temperature data for 50.0 per cent Y-Lu alloy.

Fig. 5. Resistivity versus composition isotherms for Gd-Lu alloys.

Fig. 6. Resistivity versus composition isotherms for Tb-Lu alloys.

Fig. 7. Resistivity versus composition isotherms for Gd-Er alloys.

temperatures illustrates the necessity for measurements at low temperatures if one wishes to make a meaningful comparison of resistivity data with Nordheim's rule. The unsymmetrical shape of the curves for these alloy systems is due to the presence of magnetic scattering and the large difference between the temperature coefficient of the resistivity above and below the magnetic ordering temperature. This behavior is in direct contrast to that found in Ni-Pd alloys⁽³⁾ where such curves were unsymmetrical at low temperatures and symmetrical at temperatures above the ordering temperatures of all the alloys.

The spin-disorder resistivities give a measure of the magnetic interaction in the metal. They were evaluated by extrapolating from

Table 2. Magnetic ordering temperatures observed
in resistivity-temperature curves

Alloy	θ	θ' *
80.2 Gd-Lu	240	
57.3 Gd-Lu	167	
40.2 Gd-Lu	121	
20.0 Gd-Lu	61	
93.4 Tb-Lu	211	181
66.7 Tb-Lu	157.5	
46.7 Tb-Lu	120	
23.3 Tb-Lu	63.5	
81.8 Gd-Er	261.5	
63.7 Gd-Er	225.5	
45.0 Gd-Er	170.5	138
25.7 Gd-Er	128.5	70
Gd†	291.5	
Tb†	229	219
Er†	80	200

* Possible antiferromagnetic-ferromagnetic transition.

† Data from Reference 5.

linear portion of the ρ -T curves in Figs. 1-3 to $T=0^\circ\text{K}$. Figure 8 shows that these values for the alloys follow the $(g-1)^2 J(J+1)$ relation (or $S^2(J+1)/J$ for the heavy rare earths) about as well as do the metals themselves. The values of S and J for the alloys were determined from the S and J of the metals by multiplying by the mole fraction of each component in the alloy as done by Weiss and Marotta.⁽⁷⁾ The fact that all the points do not fall on a straight line is believed to be a function of the variations in electronic structure of the metals rather than a weakness in the assumption that the spin disorder resistivities should follow a $(g-1)^2 J(J+1)$ dependence.⁽⁸⁾ Experiments on dilute alloys have shown that this relation is obeyed quite well where the electronic structure remains essentially constant.⁽⁹⁾

ALLOY STUDIES

The residual resistivity of a solid solution alloy at absolute zero is usually caused by scattering of conduction electrons by two mechanisms, imperfections in the lattice and the difference in electrostatic potential of the two types of atoms in the alloy. The first type is the same as that found in pure metals and includes scattering by dislocations, grain boundaries, impurity atoms etc. The second type could actually be treated as a very large concentration of impurity atoms but in alloys it is usually treated separately and described by Nordheim's

Fig. 8. Spin disorder resistivities for the alloys and pure metals as a function of average values of $S^2(J+1)/J$.

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rule, $\rho = Cx(1-x)$, where x is the mole fraction of one component and C is a constant dependent on the difference in the electrostatic potential of A atoms and B atoms.

The alloys examined in this study had much larger residual resistivities than one would expect for alloys with similar electronic structures, crystal structures and atomic sizes (c.f. Ag-Au and Pt-Pd⁽¹⁰⁾), and the magnitude of the residual resistivity at a given composition depended upon the difference in angular momentum quantum number of the alloy components. The additional contribution to the resistivity is due to a type of spin disorder scattering of the conduction electrons found only in alloys where one or more of the components has a localized magnetic moment. The effect is similar to that giving rise to the magnetic anomaly in the pure metals, where no scattering occurs at 0°K, but disorder of the spins with increasing temperature causes a disruption of the perfect periodicity of the lattice and hence scattering and an increase in resistivity. The effect in alloys, however, is present even at 0°K where the spins are completely aligned, for the disorder of the atoms with magnetic moments in the lattice is still a disruption of the periodicity of the lattice. Thus the residual resistivity in these alloys is composed of three parts,

Thus the residual resistivity in these alloys is composed of three parts, $\rho_{\text{residual}} = \rho_{\text{imp}} + \rho_{\text{AE}} + \rho_{\text{AS}}$, the imperfection resistivity, the electrostatic effects of alloying, and the spin disorder effects of alloying, respectively. The temperature dependent part of the resistivity in the alloys, as in a magnetic rare-earth metal, consists of a thermal vibration or phonon contribution and a spin disorder contribution below the magnetic ordering temperature, and only the phonon term above the ordering temperature.

A qualitative idea of the magnitudes of the various terms in the residual resistivity is provided by a comparison of the results from a 50 per cent Y-Lu alloy (with no magnetic term) with the results for Gd-Lu and Tb-Lu at the same composition. A more quantitative evaluation is possible with dilute alloys as described elsewhere by Mackintosh and Smidt.⁽⁹⁾ That work showed the electrostatic term for elements in the sixth period is less than the term for an alloy between a fifth period and sixth period element (Y-Lu). This difference is simply the "a" term in Linde's rule for dilute alloys, $\Delta\rho = a + bz^2$. The rare-earth alloys studied had no bz^2 term because the valences were the same, but would require an additional term $c(g-1)^2 J(J+1)$ to describe the properties of dilute rare-earth alloys in lutetium; g is the Landé factor, J is the total angular momentum quantum number, and c is a constant.

Mott and Stevens⁽⁴⁾ suggested that the localized electron and collective electron models for magnetism in metals should influence the resistivity in different ways which would be evident in a comparison of

the resistivities of a metal and one of its alloys with a paramagnetic metal. The ρ -T curves for a metal and an alloy of the localized electron type should have similar slopes above and below the ordering temperature while for the collective electron case the slopes for the metal and the alloy should differ above the ordering temperature if there were a difference in the number of unfilled d states at the Fermi level into which s electrons could be scattered. This proposal was tested for the localized electron model by a comparison of Gd and an 80.2 per cent Gd-Lu alloy for which the curves superimposed quite well as shown in Fig. 9. The small deviations noted can be explained by slight differences in the Fermi surfaces of Gd and Lu as discussed in the next section.

ELECTRONIC STRUCTURE OF THE RARE-EARTH METALS

Although the rare-earth metals are generally considered to be identical in possessing three conduction electrons (with the exception of Eu, Yb, and ϵ -Ce), a closer scrutiny of the resistivity data on the metals^(6, 11) shows rather sizeable differences in the ρ -T curves in the paramagnetic region. This would indicate rather large variations in some of the parameters in the electrical transport equations and suggested a further analysis of the data on the pure metals as well as those obtained from the alloys.

The Bloch-Gruneisen relation predicts a T^5 temperature dependence for metals at low temperatures and a linear dependence for $T > \theta$. White and Woods⁽¹²⁾ have found that the transition metals more generally follow a T^3 dependence in the low temperature region and a similar

Fig. 9. Reduced resistivity versus reduced temperature curves for Gd and 80.2 per cent Gd-Lu alloy.

analysis of the data on rare-earth metals showed the same trend.

Table 3 shows the coefficient of T in the expression $\rho = cT^n$ as determined by plotting $\log \rho$ versus $\log T$. The T^2 dependence of ytterbium and europium is perhaps notable but no low temperature data on other cubic divalent metals could be found so it is not known if this effect is typical of divalent metals.

A possible explanation of the T^3 behavior in the magnetic metals has been given by Kasuya⁽¹³⁾ as well as others, who have derived a T^2 term for a ferromagnetic and a T^4 term for an antiferromagnetic metal using a spin wave model. Magnetic anisotropy effects⁽¹⁴⁾ and electron-electron⁽¹⁵⁾ interactions probably modify this dependence, however. In addition it is difficult to accept this interpretation when Sc,⁽¹⁶⁾ Y, Lu, and La, which are all weakly paramagnetic, also have a T^3 dependence, while in contrast to the behavior of these metals an alloy, 50 per cent Y-Lu, followed a T^5 dependence very well.

Table 3. Summary of temperature dependence of the resistivity in the low temperature region

Material	n	Material	n	n'
Gd	3.0 (10-40)*	80.2 Gd-Lu	3.5 (6-16)*	2.8 (17-35)*
Tb	3.2 (14-35)	57.3 Gd-Lu	4.1 (7-15)	2.6 (21-41)
Dy	3.3 (10-32)	40.2 Gd-Lu	6.3 (11-14)	2.4 (14-37)
Ho	2.3 (13-19)	20.0 Gd-Lu	6.0 (6-10)	2.2 (15-40)
Er	3.5 (6-18)	93.4 Tb-Lu	4.3 (11-18)	2.9 (18-34)
Tm	4.5 (6-21)	66.7 Tb-Lu	6.1 (11-17)	2.9 (17-35)
Yb	2.0 (14-40)	46.7 Tb-Lu	4.6 (8-17)	2.5 (17-37)
Lu	2.6 (18-40)	23.3 Tb-Lu	6.6 (7-10)	2.8 (12-29)
Sc†	3.7 (15-28)	81.8 Gd-Er	4.2 (6-13)	2.5 (13-37)
Y	3.1 (11-40)	63.7 Gd-Er	4.2 (8-19)	2.3 (19-40)
La	2.6 (9-26)	45.0 Gd-Er	3.4 (9-15)	2.2 (17-35)
Sm	3.5 (3-14)	25.7 Gd-Er	4.4 (6-13)	2.2 (20-35)
Eu	1.8 (14-32)	50.0 Y-Lu	5.0 (11-22)	2.2 (22-56)

* Temperature range in which n is observed.

† Data from Reference 16.

One other feature of the temperature dependence of the resistivity of the rare-earth metals was noted in a qualitative comparison of the curves. The light rare earths, La, Ce, Pr, and Nd, do not follow a linear relation very well above θ , while the heavy rare earths, Gd to Lu and also Y and Sc, follow such a relation quite well. The essential differences between these two groups are the amount of shielding by the 4f shell and the more complex crystal structure of the light rare earths.

Ziman⁽¹⁵⁾ has shown that the Fermi surface area can be estimated from the resistivity in the linear region ($T > \theta$) (or the temperature coefficient of the resistivity in this region), using a parameter R , where

$$R = 8.125 \times 10^9 \left[\frac{M\theta^2\rho}{DT} \right] ;$$

M being the atomic weight, θ the Debye temperature, ρ the resistivity due to lattice vibrations, D the Debye radius, and T the temperature at which ρ is measured. R is proportional to $n^{2/3} (S_{\text{free}}/S)$ where n is the number of conduction electrons and S and S_{free} are the areas of the actual and free electron Fermi surfaces respectively. A comparison of the calculations with anomalous skin effect measurements on metals where the Fermi surface geometries have been determined, shows that the constant of proportionality is 1 for the third period elements but appears to be smaller for other periods. ⁽¹⁷⁾

The values of this parameter for the rare-earth metals were estimated after correcting for the spin disorder contribution as previously described. These values are shown in Table 4 as well as the ratio S/S_{free} , while a comparison with other metallic elements is shown

Table 4. Electronic structure parameters derived from
Ziman's equations

Metals	R	S/S_{free}	N_{eff}
La	30.9	.259	.40
Ce	36.2	.239	.35
Pr	23.6	.297	.49
Nd	24.8	.289	.47
Sm	37.4	.235	.34
Eu*	14	.34	.4
Gd	13.6	.375	.69
Tb	23.0	.301	.50
Dy	27.7	.274	.43
Ho	39.2	.230	.33
Er	55.1	.194	.26
Tm	49.8	.204	.28
Yb	9.6	.407	.52
Lu	54.8	.195	.26
Sc*	52	.20	.3
Y	53.6	.197	.26

*R values calculated with values of θ estimated from Lindeman melting point formula (Eu - 94°K, Sc - 308°K). Reference 16 calculated an R value for Sc of 69.0 using a different value of θ .

in Fig. 10. A value for the number of effective electrons, which gives an indication of the fit to the transport equations, has also been calculated from Ziman's equations and is tabulated in Table 4.

The absolute values of these parameters may of course be in error because of the uncertainty in the proportionality constant, but the relative values within the rare-earth series are significant and represent facts which remain to be explained. Estimates of R were also made for the alloys assuming a linear change of M, θ , and D across the alloy system and are shown in Fig. 11.

Fig. 10. Ziman R parameter for metallic elements. Values taken from Reference 15 except for Mn, V, Re, and Hf which were calculated from data given in Reference 12 and the rare earths.

Fig. 11. Variation of Ziman R parameter in alloy systems Gd-Lu, Tb-Lu, and Gd-Er.

The most striking feature of these calculations of R is the wide variation across the heavy rare-earth series. Mackintosh⁽¹⁸⁾ has suggested that the Fermi surface for these metals might be roughly approximated by the free electron Fermi surface. If the transport properties of these metals are dominated by the large piece of Fermi surface in the third Brillouin zone a correlation with the change of c/a ratios for these metals is possible. As the c/a ratio decreases from Gd to Er this surface would shrink and the conductivity would decrease while the increase in c/a ratio for Tm and Lu would produce an increase in the area of this surface and hence in the conductivity.

CONCLUSIONS

Studies of alloy systems among the heavy rare-earth metals have shown that there is a sizeable contribution to the residual resistivity when one or more of the components is magnetic. This contribution results from the random distribution of atoms with localized moments through the lattice.

At temperatures above the ordering temperature of a rare-earth metal or alloy the spin disorder resistivity can be separated from the total to obtain the lattice resistivity. Sizeable variations in the magnitude of the lattice resistivity are shown to be qualitatively correlated with the change in c/a ratio across the heavy rare-earth series, and the attendant modification thus produced in the Fermi surface.

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FIGURE CAPTIONS

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- Fig. 2. Resistivity versus temperature data for Tb-Lu alloys.
- Fig. 3. Resistivity versus temperature data for Gd-Er alloys.
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