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EFFECTS OF DILUTE RARE-EARTH ADDITIONS
ON THE ELECTRICAL CONDUCTIVITY OF CERIUM AT LOW TEMPERATURES*

F. W. Clinard, R. O. Elliott, and W. N. Miner

University of California, Los Alamos Scientific Laboratory,
Los Alamos, New Mexico

84796

ABSTRACT

Two atomic percent of the various trivalent rare earths were dissolved in cerium, and the electrical resistivities of these dilute binary alloys evaluated in the range 1.5 to 297°K, in order to determine whether the various solute magnetic properties might be reflected in resistivity measurements. It was found that the γ and β phases at room temperature showed a roughly linear dependence of resistivities on atomic number of solute species, with a slight effect attributed to solute-solvent atomic size mismatches. At 4°K the resistivities of predominantly α phases were found to be influenced by the presence of small amounts of β , and predominantly β phases by small amounts of α . Spin-disorder resistivities for β phase were found to be a nearly linear function of atomic number of solute, and did not clearly reflect the influence of any solute magnetic parameters. A slight decrease in spin-disorder resistivities was noted in the direction of the heavier rare earth solutes.

INTRODUCTION

The element cerium can exist in three phases between room temperature and 0°K. After being annealed at high temperature, the room temperature crystal structure is fcc (γ phase), with a lattice constant of 5.16 Å. Cerium in this form has about 0.9 $4f$ electron per atom. On

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cooling, the γ phase transforms partially to the hcp β form, but the number of $4f$ electrons is unchanged. With further cooling, the untransformed γ phase undergoes an electronic transformation to a more dense fcc form, designated α phase. This structure has a lattice parameter of 4.85 Å, and about 0.4 $4f$ electron per atom. With still further cooling, the β phase transforms to the α phase, thus undergoing both a crystallographic and an electronic transformation. These low-temperature cerium phases have been more completely described by Gschneidner.⁽¹⁾

Repeated thermal cycling of annealed samples between room and liquid helium temperatures can increase the amount of β to the point where it is predominant in this temperature range.⁽²⁾ The β phase of cerium transforms from the paramagnetic to the antiferromagnetic form, at 12.5°K.⁽³⁾

Previous experimental findings on cerium containing small amounts of other rare earths suggest that the electrical conductivity of such binary solid solution alloys may be a function of solute species. Gschneidner et al.⁽⁴⁾ reported that the temperature of the $\gamma \rightarrow \alpha$ cerium transformation, which involves a change in electronic configuration is strongly dependent on the specific rare earth alloying element at the 2 a/o level. In explaining this effect, they postulated that the spin of the unpaired $4f$ solute atoms was primarily responsible for the observed dependence. Their conclusion resulted from the observation that the change in transformation temperature as a function of the atomic number of the rare earth solute was reciprocally related to the spin of the solute atoms. The mechanism by which transition temperatures were lowered was believed to involve an indirect interaction between the unpaired $4f$ electron of the cerium and those of the solute atoms via the conduction electrons.⁽⁴⁾ This suggestion that conduction electrons might play a part in the observed variation of transformation temperature as a function of solute species in cerium led to the present experiment, in which the resistivity of cerium plus 2 a/o rare earth additions has been determined as a function of temperature between 1.5 and 297°K. The present paper deals with the resistivities of these dilute alloys at room

temperature and at liquid helium temperatures.* Data are reported as a function of atomic number of solute, in order to determine the possible effect of various solute magnetic parameters on the resistivities of the alloys. Phases considered are: γ at 297°K, β at 297°K, β at 4°K, and α at 4°K. Only the β alloys at 297°K were thought to be single phase (i.e., phase pure). The other phases listed were the predominant ones in two-phase mixtures.

It is worth emphasizing that the cerium alloys dealt with here were quite dilute. Only one solute atom was present for every 50 solvent atoms.

Only one other investigation of the effect of a series of dilute solutions of rare earths in another rare earth on the electrical resistivities of the alloys has come to our attention. Mackintosh and Smidt⁽⁵⁾ have reported residual resistivities of lutetium containing small percentages of gadolinium, terbium, dysprosium, holmium and erbium. They concluded that the change in residual resistivity per atomic percent of solute added is a function of the factor $(g-1)^2 J(J+1)$, where g is the Landé factor and J is the localized ionic moment of the solute.

EXPERIMENTAL PROCEDURE

The eleven alloys discussed here were made from cerium stock which was estimated by difference to be 99.75 w/o pure. The major metallic impurities were 0.1 w/o lanthanum, 0.05 w/o manganese, and 0.05 w/o iron. Major non-metallic impurities were 235 ppm carbon, 115 ppm hydrogen, 30 ppm nitrogen, and 80 ppm oxygen. The resistivity of the cerium stock at 3.96°K (the normal boiling point of liquid helium at Los Alamos) was $7.14 \mu\Omega\text{-cm}$.

Most of the alloys were arc-cast, swaged from about 0.312 to 0.265 in. diameter, heat treated, and then machined into the final rod-shaped

*The effects of the normally trivalent rare earth solutes are reported here. The normally divalent elements europium and ytterbium will be discussed at a later date.

form. Final sample dimensions were 0.250 in. diameter by 1.125 in. long. Potential probe separations for electrical resistivity measurements were about 1.5 cm.

Arc-cast alloys containing dysprosium, erbium and thulium were not swaged, but were induction cast to the approximate final shape in a helium atmosphere. The casting technique was to force the molten alloy up into a 0.275 in. ID tantalum tube immersed in the melt, by means of helium admitted to the previously evacuated furnace (manometric casting method). The tantalum tube was subsequently machined from the casting, and the specimen reduced to its final dimensions by further machining after heat treatment.

The alloys were homogenized and annealed in the following manner. Each specimen was wrapped in tantalum foil and sealed within a Pyrex capsule under 0.3 atm of argon. The capsules were then placed in a furnace at 525°C (about 0.7 of the melting point) for approximately 300 hr. At the end of this period, the capsules were removed from the furnace and cooled rapidly (about 100°K/min) to room temperature. The specimens were then broken out of the capsules and machined to their final dimensions. Specimen densities were determined at this time, and these γ -phase values are reported in Table I.

The machined specimens, four at a time, were loaded into the copper block specimen holder of the resistivity apparatus, and their resistivities measured at 297°K. These data are reported as the gamma curve of Fig. 1(a).

Cooling to liquid helium temperatures was then carried out in the following manner. The assembly containing the specimens was pre-cooled rapidly in liquid nitrogen and, after the nitrogen had been removed, was quenched with liquid helium. The liquid nitrogen pre-cool was utilized to minimize subsequent liquid helium boil-off. The time required for cooling from 297 to 4°K was typically 2 hr. This rapid cooling was utilized to favor the formation of α . It has been reported that slow cooling enhances the formation of β phase,⁽⁶⁾ which is slower than γ to transform to α on further cooling.⁽¹⁾

Resistivity data taken at 4°K on such predominantly alpha-phase samples are shown by the "alpha" curve of Fig. 1(b). Pumping was then employed to reduce the temperature of the liquid helium to approximately 1.5°K. A resistance heater imbedded in the copper specimen holder was used to warm the specimens from this temperature to 297°K at about 0.5°K/min.

Specimens to be evaluated in the β -phase condition were given the following thermal cycling treatment after being heat treated and before being inserted in the resistivity apparatus. Each was sealed within a Pyrex capsule under 1 atm of helium and then thermally cycled 24 times from room - to liquid helium - to room temperature. The procedure for one cycle involved immersing the capsule in liquid helium, holding it in the liquid for 15 min, and then removing it for warming to room temperature over a 15 min period. Specimen densities were determined after 24 cycles, and these β -phase values are given in Table I.

The β samples prepared in the above manner were loaded into the apparatus and their resistivities measured at 297°K. These values are reported in the beta curve of Fig. 1(a). They were then slowly cooled at a rate of about 0.5°K/min to about 40°K, quenched with liquid helium, and the helium pumped to approximately 1.5°K. Specimen resistivities were determined at the liquid helium isotherm of 4°K and are given by the "beta" curve of Fig. 1(b). As was the case for the alpha specimens, the apparatus heater was utilized to warm the specimens to 297°K at a rate of about 0.5°K/min.

Resistivity data were taken manually during all runs, a potentiometric circuit⁽⁷⁾ being utilized. Voltage drops, which were later converted to resistivities, were read with a Rubicon Type B potentiometer. The sensitivity of this circuit was such that resistivity changes as small as 5×10^{-8} ohms were reliably detected.

Two methods of measuring temperature were used. In the range between room temperature and 16°K, temperatures were obtained by averaging the results from two calibrated copper-constantan thermocouples whose measuring junctions were soldered to the copper specimen holder.

The accuracy was estimated to be $\pm 0.5^\circ\text{K}$. In the range between 50 and 1.5°K , a calibrated germanium resistance thermometer was used, which had an estimated accuracy of $\pm 0.1^\circ\text{K}$. Its temperature measuring element was clamped to the specimen holder.

RESULTS AND DISCUSSION

Measured resistivities of cerium-rich alloys at 297°K as a function of rare earth solute species are shown in Fig. 1(a). The lower curve represents samples in the annealed condition. Density measurements, shown in Table I, indicated that most of these specimens were primarily γ phase, although the observed trend toward increasing density with increasing atomic number of the solute was not continued for the solutes erbium, thulium and lutetium. This failure to follow the trend was attributed to the likely formation of a small amount of beta phase in these three alloys. The upper curve of Fig. 1(a) represents resistivities of the cerium alloy samples at 297°K after they had been thermally cycled 24 times to 4°K to transform them as completely as possible to β . The trend in density measurements (Table I) and subsequent resistivity-temperature curves indicated that the cycled specimens consisted entirely of β at room temperature. It may be seen in Fig. 1(a) that the resistivities of both γ and β phases are linear functions of the atomic numbers of rare earth solutes.

The results shown in Fig. 1(a) indicate that at room temperature the magnetic properties of the various rare-earth solute species dissolved in cerium to the extent of 2 a/o have no appreciable effect on the electrical resistivity of the alloys. The slight linear rise in resistivities as a function of atomic number of solute is probably attributable to lattice strains resulting from differences between the atomic sizes of the solvent and solutes. Since in both the γ and β phases the cerium atoms are trivalent,⁽⁸⁾ the effect of the lanthanide contraction in the other trivalent rare earths is to cause the greater size mismatch to occur with the heavier rare earth solutes. This would then lead to higher resistivities for those alloys near the lutetium end of the series, as was found experimentally.

Measured resistivities at 4°K are shown in Fig. 1(b). The lower curve represents measurements on specimens cooled rapidly to liquid helium temperature from the annealed state. It might be inferred from this curve that the resistivities of these samples, which were predominantly α phase, is a function of some solute property which relates to a minimum near neodymium or samarium. However, examination of the curves of resistivity as a function of temperature for the various samples heated slowly from 4°K indicated that this was not the case. Instead, it appeared that the resistivity variation as a function of atomic number of solute was due to the different percentages of β phase present in these otherwise α alloys at 4°K. It was possible from examination of the heating curves to make a crude estimate of the amount of β present in the α phase, by observing the magnitude of the resistivity change at the Néel point of the β phase. The smallest discontinuities occurred at about samarium or gadolinium in the series, and the largest at lanthanum and lutetium. Thus, with regard to the "alpha" curve in Fig. 1(b), we conclude that the various amounts of high-resistivity β phase present in the predominantly α -phase specimens may have obscured any possible contributions due to magnetic properties of the rare earth solutes.

The upper curve of Fig. 1(b) represents resistivities of the cerium alloy samples at 4°K after 24 thermal cycles to that low temperature. The departure of this curve from a straight line can largely be attributed to a lack of phase purity. It was found from examination of the resistivity vs. temperature curves of these predominantly β samples that some α phase formed on cooling at low temperatures but reverted to β phase on warming, so that the samples at room temperatures were always in the β form. The amount of α present in these samples at 4°K (as deduced from the resistivity-temperature curves) was greatest at samarium and least at lanthanum and lutetium. Thus the presence of some low-resistivity α phase in the predominantly β samples would, at least in part, account for the shape of the curve.

We think that the resistivities of the predominantly β samples at

4°K can be roughly corrected for α -phase effects, since the percentages of α from sample to sample appeared to be rather small. The corrections would tend to straighten the "beta" line shown, so that a straight line would approximate the corrected data. A straight line suggests that at low temperatures the magnetic properties of the rare-earth solutes in β cerium have no major effect on the electrical resistivities of the alloys. A rise in resistivities toward the heavy end of the series is observed, as was seen at higher temperatures, and may be attributable to size effects. The magnitude of the effect at low temperatures, however, is larger than was found at room temperature (Fig. 1(a)).

We have thus far discussed only the measured values of electrical resistivity as a function of solute species in our attempt to determine the effect of the magnetic properties of the solute atoms on resistivities of the alloys. Of more fundamental significance are the results of an examination of spin-disorder resistivity, since this parameter is not as subject to secondary influences as is measured resistivity. Spin-disorder resistivity is defined here as the difference between the paramagnetic resistivity and the residual resistivity, both extrapolated graphically to 0°K. The paramagnetic resistivities were extrapolated from the linear paramagnetic regions in the resistivity-temperature curves; the residual resistivities were extrapolated from the resistivity data obtained at the lowest temperatures.

Spin-disorder resistivities were thus obtained from the resistivity-temperature plots of the predominantly β samples, which ordered magnetically at $\sim 17^\circ\text{K}$. The parameters used to calculate spin-disorder resistivity, and the results obtained, are shown in Table II. Spin-disorder resistivity as a function of atomic number of solute is shown in Fig. 2. The dip in the curve at samarium is partially due to the presence of a relatively high percentage of α phase, as discussed earlier. Our experimental evidence indicates that the spin-disorder resistivity, if present at all, is lower in α phase than in β . However, a rough correction to remove the effects of the various amounts of alpha present in the β specimens did not change the overall shape of the curve. It

thus appears that the true curve for spin-disorder resistivity as a function of atomic number of solute would have slight dips near the center and at the ends of the series, somewhat reminiscent of the variation of the magnetic parameter $L(L+1)$ across the rare earth series, where L is the total orbital angular momentum. The magnitude of the dips, however, is about the same as that due to experimental scatter. The only trend clearly established in this experiment was a slightly negative slope toward the heavier rare earths.

The present findings show no clear variation of resistivities with any magnetic parameter across the rare earth series. If such a dependence does exist, it is likely that it could be unambiguously detected by the present technique only if a higher percentage of solute were present. Such solute concentrations, however, were not required in the experiments of Mackintosh and Smidt,⁽⁵⁾ who added small percentages of heavy rare earths to lutetium and found significant changes in residual resistivities which they correlated with the magnetic parameter $(g-1)^2 J(J+1)$. Smidt and Daane,⁽⁹⁾ when they alloyed rare earths with other rare earths, found large variations in spin-disorder resistivities and a correlation with the term $(g-1)^2 J(J+1)$. Their experiments are not directly comparable with ours, however, since they examined much higher solute concentrations. They also found that the magnetic ordering temperatures varied greatly with alloying content. In the present experiment negligible variations in β -phase Néel temperatures across the rare-earth solute series were found, an observation consistent with the absence of any detectable dependence of resistivity on magnetic parameters.

The same cerium-rich compositions discussed here were found by Gschneidner et al⁽⁴⁾ to show a solute spin-dependent effect on the $\gamma \rightarrow \alpha$ transformation temperatures. It is not clear why a similar effect was not observed in the present electrical resistivity data if the conduction electrons are involved in the coupling of the $4f$ electrons.

The negative slope seen in the plot of spin-disorder resistivity as a function of increasing solute atomic number (Fig. 2) is rather minor. It may be related to the observation⁽¹⁰⁾ that the energetically deep $4f$

shells in the heavier rare earths are highly localized and do not interact strongly, whereas the energy levels for the $4f$ electrons in the lighter rare earths are closer to those for the $5d$ $6s$ states, and thus may interact to some extent. From this view, the magnetic interaction of solvent and solute atoms by the Friedel-Rocher mechanism of virtual bound states^(10,11) might be expected to be less with heavy rare earth solutes, and thus decrease spin-disorder resistivity when these elements are present in cerium. It is also possible that the negative slope in Fig. 2 may be due to changes in band structure or Fermi level as alloying elements are added to cerium.

SUMMARY

Two atomic percent of the various trivalent rare earths were dissolved in cerium, and the electrical resistivities of these dilute binary alloyw determined in the range 1.5 to 297°K. Resistivities are reported for: predominantly γ phase at 297°K, β phase at 297°K, predominantly α phase at 4°K, and predominantly β phase at 4°K.

Resistivities at 297°K for both γ and β phases were found to be a linear function of atomic number of solute, with a slight increase toward the heavy rare earths being attributed to atomic size effects.

Resistivities for predominantly α -phase samples at 4°K were found to be influenced significantly by the percentages of β phase retained on cooling. β -phase resistivities at 4°K were also affected by small amounts of α phase present.

Spin-disorder resistivities were determined for the predominantly β samples and were found not to reflect the influence of solute magnetic parameters that had been suggested by the work of others. A slight downward trend in spin-disorder resistivities was detected with increasing atomic number of solute, and is considered in terms of a virtual bound state model.

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Table I. Room-temperature gamma and beta phase densities of cerium containing 2 a/o of various other rare earths. (Density determination by an immersion method.)

Solute	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm	Lu
γ -phase density* (g/cm ³)	6.73	6.75	6.76	6.76	6.77	6.77	6.78	6.78	[6.77]	[6.78]	[6.77]
β -phase density (g/cm ³)	6.67	6.69	6.70	6.71	6.71	6.72	6.72	6.72	6.73	6.73	6.74
Density diff.	0.06	0.06	0.06	0.05	0.06	0.05	0.06	0.06	0.04	0.05	0.03

* Brackets indicate uncertainty in phase purity.

Table II. Resistivities of cerium, predominantly beta phase, containing 2 a/o of various other rare earths. (Units of ρ are $\mu\Omega$ -cm.)

Solute	La	Pr	Nd	Sm	Gd	Tb	Dy	Ho	Er	Tm	Lu
ρ at 4°K	16.8	15.0	16.6	19.0	24.6	25.0	24.4	27.5	24.0	26.2	30.1
Paramagnetic ρ extrap. to 0°K	49.8	47.7	47.8	46.9	52.3	54.0	52.7	56.3	53.2	55.5	57.0
Residual ρ extrap. to 0°K	15.1	12.9	14.4	17.0	22.5	22.9	22.6	25.6	22.1	24.4	28.2
Spin-disorder ρ * at 0°K	34.7	34.8	33.4	29.9	29.8	31.1	30.1	30.7	31.1	31.1	28.8

* The spin-disorder resistivity was obtained by subtracting the residual resistivity from the paramagnetic resistivity, both extrapolated to 0°K.

FIGURE CAPTIONS

- Fig. 1. Resistivities of cerium containing 2 a/o additions of various other rare earths. Quotation marks around the words alpha and beta indicate uncertainty in the phase purities of these alloys.
- Fig. 2. Spin-disorder resistivity of beta cerium (containing 2 a/o additions of various other rare earths) as a function of the atomic number of solute. Quotation marks around the word beta indicate an uncertainty in the phase purity of these alloys.

Figure 1.

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Figure 2.

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