

## Resistivity of Very Pure Th and Th-Rare-Earth Alloys\*

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Resistivity data are given for pure thorium samples with a resistivity ratio  $[\Gamma = \rho_{300^\circ\text{K}}/\rho_{4.2^\circ\text{K}}]$  greater than 1000. At high temperatures, deviations of the resistivity from the Bloch-Grüneisen relation correspond closely to the anomaly which is found in the specific heat. The resistivity at 300°K is found to be 15.8  $\mu\Omega\text{-cm}$ . Thorium-rare-earth alloys show no resistance minimum of the type discussed by Kondo, to an accuracy of 0.001  $\mu\Omega\text{ cm}$ .

### INTRODUCTION

METALS which contain a dilute solution of magnetic impurity often show a minimum in the electrical-resistance-versus-temperature curve. Extensive studies<sup>1</sup> of the 3-*d* transition-metal impurities in a nonmagnetic host have shown a high correlation between the occurrence of a minimum and the occurrence of a local moment. Recently, Kondo<sup>2</sup> has advanced a theory to explain these experiments which gives a spin-scattering resistivity proportional to the logarithm of the temperature. In most cases the agreement of this theory with experiment is good.<sup>2,3</sup> The rare earths are well suited for an extension of these studies because they are known to retain a moment in metallic hosts.<sup>4</sup> Sugawara and co-workers have investigated dilute solutions of the rare earths in La<sup>5</sup> and Y<sup>6</sup> and find a minimum for La-Ce and Y-Ce. The other alloys show a resistivity  $\rho$  which decreases monotonically with decreasing temperature  $T$ . Within the framework of the Kondo theory, these results can be interpreted to give the sign and magnitude of the coupling constant  $J$  between the impurity spin and the conduction-electron spin.

Resistivity data are presented here for a series of thorium-rare-earth alloys. Results are discussed in terms of the Kondo theory and the strength of the impurity-conduction-electron coupling. In addition, we report resistivity measurements for thorium of much higher purity than any previously published.

### EXPERIMENTAL

Resistivities were measured by a standard four-probe technique with knife-edge contacts. A Guildline type 9180-B potentiometer and galvanometer-amplifier were used to detect the voltages. All electrical leads were

thermally anchored to a large copper yoke which completely surrounded the sample. Thermal equilibrium was maintained with a standard heat-leak chamber<sup>7</sup> and temperatures were measured with a copper-versus-constantan<sup>8</sup> or gold-iron-versus-copper<sup>9</sup> thermocouple.

### Pure Thorium

Significant progress has been made in the purification of Th. An electrotransport process<sup>10</sup> in a vacuum of  $10^{-9}$  Torr consistently gives samples with resistivity ratios ( $\Gamma = \rho_{300^\circ\text{K}}/\rho_{4.2^\circ\text{K}}$ ) of approximately 1000. Existing analytical techniques are not sufficiently sensitive to measure the impurities in these samples but the nitrogen content was less than 3 ppm and the iron less than 5 ppm. Carbon is one of the major impurities in thorium and is the most difficult one to remove by electrotransport. A series of samples were prepared by adding measured amounts of carbon to thorium. The residual-resistivity results, shown in Fig. 1, indicate that the residual resistivity is directly proportional to the carbon concentration with a slope of  $5.5 \times 10^{-3}$

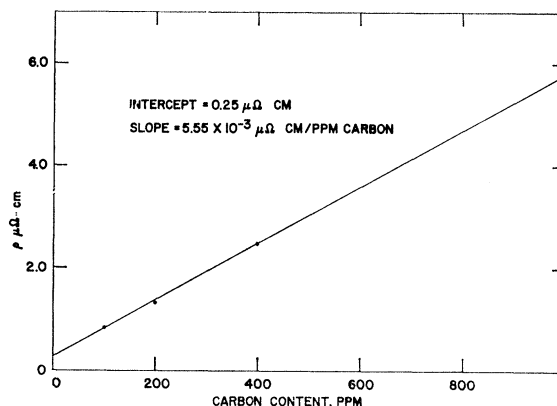


FIG. 1. Variation of the residual resistivity of thorium with carbon content.

\* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1926.

<sup>1</sup> G. J. van den Berg, in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1964), Vol. VI.

<sup>2</sup> J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32, 37** (1964); **34, 204** (1965); **34, 523** (1965).

<sup>3</sup> M. P. Sarachik, *Phys. Rev.* **137, A659** (1965).

<sup>4</sup> F. H. Spedding, S. Legvold, A. H. Daane, and L. D. Jennings, in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. II.

<sup>5</sup> T. Sugawara and H. Eguchi, *J. Phys. Soc. Japan* **21, 725** (1966).

<sup>6</sup> T. Sugawara, *J. Phys. Soc. Japan* **20, 2252** (1965).

<sup>7</sup> D. K. Finnemore, T. F. Stromberg, and C. A. Swenson, *Phys. Rev.* (to be published).

<sup>8</sup> R. L. Powell, M. D. Bunch, and R. J. Corruccini, *Cryogenics* **1, 139** (1961).

<sup>9</sup> D. K. Finnemore, J. E. Ostenson, and T. F. Stromberg, *Rev. Sci. Instr.* **36, 1369** (1965).

<sup>10</sup> D. T. Peterson, F. A. Schmidt, and J. D. Verhoeven, *Trans. AIME* **236, 1311** (1966).

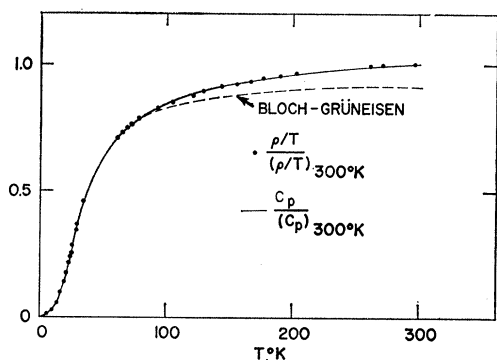


FIG. 2 Resistivity of pure thorium ( $\rho/T$  versus  $T$ ). Data above  $78^\circ\text{K}$  were taken for sample 244; data below  $78^\circ\text{K}$  were taken for sample 230. The normalized specific heat follows  $\rho/T$  to an accuracy of 1%.

$\mu\Omega$  cm/ppm carbon. Sample 244 has a residual resistivity of  $0.0187 \mu\Omega$  cm and, if all of this were due to carbon, would be expected to contain 3.4 ppm of carbon.

The resistivity results on this high-purity thorium are summarized in Table I. For sample 244, the length-to-area ratio was measured very carefully and the resistivity was found to be  $15.73 \pm 0.05 \mu\Omega$  cm at  $298.8^\circ\text{K}$ . The value,  $15.80 \mu\Omega$  cm, given in the table for  $300^\circ\text{K}$  was obtained by an extrapolation from  $298.8^\circ\text{K}$  with a slope of  $0.056 \mu\Omega$  cm/ $^\circ\text{K}$ . Sample 147A has a room-temperature resistivity somewhat higher than the other samples but the difference,  $\rho_{300^\circ\text{K}} - \rho_{4.1^\circ\text{K}}$ , is still  $15.8 \pm 0.2 \mu\Omega$  cm. Many other values for the resistivity

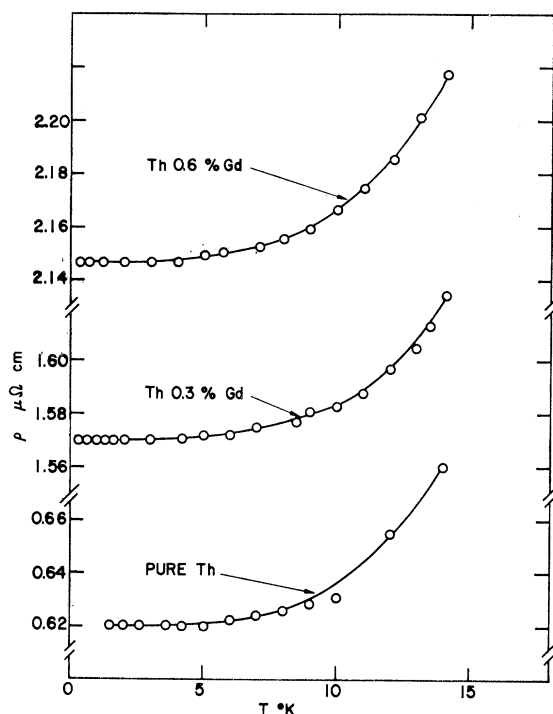


FIG. 3. Resistivity of Th-Gd alloys.

TABLE I. Resistivity of pure thorium.

Sample number	$\rho_{300^\circ\text{K}}$	$\rho_{4.2^\circ\text{K}}$	$\Gamma$	$\frac{d\rho}{dT}_{300^\circ\text{K}}$ ( $\mu\Omega$ cm/ $^\circ\text{K}$ )
244	15.80 $\pm 0.05$	0.0187	846	0.0562
230	15.6 $\pm 0.2$	0.0136	1140	0.0558
147A	16.4 $\pm 0.2$	0.62	26	0.0553

of thorium at  $300^\circ\text{K}$  have appeared in the literature<sup>11</sup> but the data reported here represent the first time consistent results have been obtained for a number of samples of very high purity and low residual resistivity. These results indicate that the resistivity of completely pure thorium at  $300^\circ\text{K}$  would be  $15.78 \pm 0.05 \mu\Omega$  cm.

The temperature dependence of the resistivity does not follow a simple theory. At high temperatures there are significant deviations from the linear dependence which can easily be seen on the ( $\rho/T$ )-versus- $T$  plot of Fig. 2. Below  $80^\circ\text{K}$  the data can be fit to the Bloch-Grüneisen equation with a Debye temperature  $\Theta_D$  of  $135^\circ\text{K}$ , but at higher temperatures the data increase more rapidly than the theory predicts. A corresponding effect occurs in the specific-heat data of Griffel and Skochdopole,<sup>12</sup> which are shown by the solid line. On

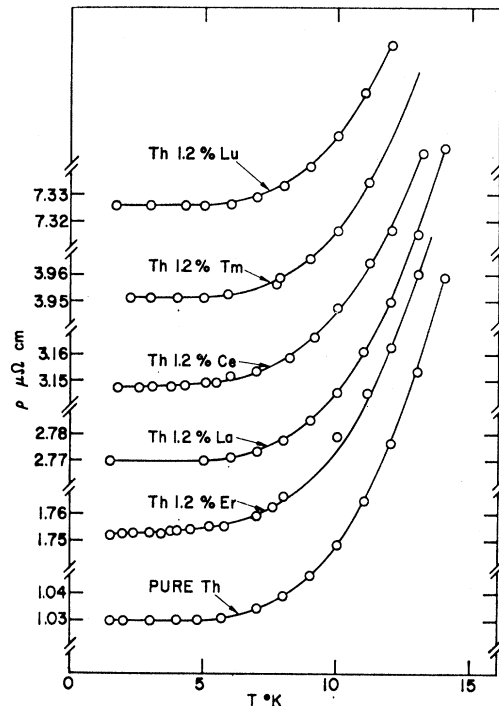


Fig. 4. Resistivity of Th-rare earth alloys.

FIG. 4. Resistivity of Th-rare-earth alloys.

<sup>11</sup> T. G. Berlincourt, *The Metal Thorium* (American Society for Metals, Cleveland, Ohio, 1958), p. 148.

<sup>12</sup> M. Griffel and R. E. Skochdopole, *J. Am. Chem. Soc.* **75**, 5250 (1963).

TABLE II. Analysis of thorium metal used for the alloys.

	Billet 159	Billet 147
Carbon	155	20
Oxygen	190	111
Nitrogen	27	20
Aluminum <sup>a</sup>	<30	<50
Chromium <sup>a</sup>	<20	<50
Iron <sup>a</sup>	<20	<50

<sup>a</sup> These values are limits of detection and the impurity content is believed to be much lower.

this reduced plot, where quantities are normalized by their value at 300°K,  $\rho/T$  follows  $C_p$  to an accuracy 1% over the entire range where thermal scattering dominates. Elcock *et al.*<sup>13</sup> have discussed effects of this sort in terms of rapid variations in the density of states at the Fermi energy. A rapid rise in the density of states at the Fermi level could easily account for the rising  $\rho/T$  and  $C_p$  at temperatures above  $\Theta_D$ . Anharmonic terms<sup>14</sup> in the lattice vibrations may be another contributing factor.

#### Thorium-Rare-Earth Alloys

Unfortunately the alloys can not be prepared by electrotransport because this process removes rare-earth ions as well as carbon and oxygen. Hence, a conventional arc-melting procedure was used. Two groups of samples are represented here; Th-Gd alloys were prepared from Th billet number 147 and all the other alloys were prepared from billet number 159. A spectrographic analysis of pure Th samples prepared from each of these billets is given in Table II. The carbon and oxygen content for both samples is much higher than for the electrotransport sample. To prepare the samples, appropriate quantities of metal to make 1.2 at.% rare-earth alloys were arc-melted 5 times, annealed at 1000°C for 2 weeks, cut, swaged, and drawn to a diameter of 0.015 in. This wire was then electropolished in a perchloric-acid-methanol solution and annealed at 800°C to remove some of the strains.

Resistivity results for the Th-Gd alloys at temperatures down to 0.3°K are shown on Fig. 3. There is no resistivity minimum to an accuracy of 0.001  $\mu\Omega$  cm

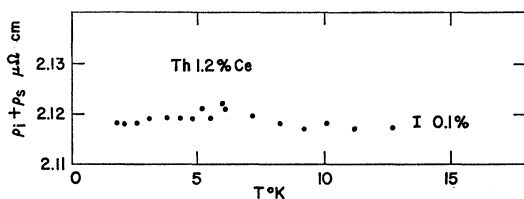


FIG. 5. Impurity resistivity for Th-Ce (total resistivity minus the resistivity of pure thorium).

<sup>13</sup> E. W. Elcock, P. Rhodes, and A. Teviotdale, Proc. Roy. Soc. (London) A221, 53 (1954).

<sup>14</sup> J. M. Keller and D. C. Wallace, Phys. Rev. 126, 1275 (1962).

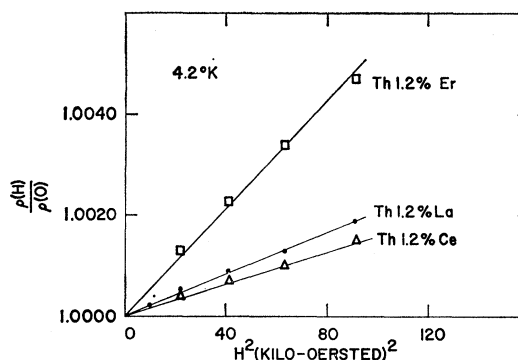


FIG. 6. Magnetoresistance of Th-Er, Th-La, and Th-Ce.

and the curvature of these plots is always positive or zero. Results for the other alloys are shown on Fig. 4. Again there is no minimum and the curvature is positive or zero. Th-Ce is of special interest because Sugawara<sup>5,6</sup> reported a strong minimum (5% of total resistivity) in La-Ce and Y-Ce. To analyze the data further we express the resistivity in terms of the four major contributions

$$\rho = \rho_0 + \rho_L + \rho_i + \rho_s,$$

where  $\rho_0$  is the residual resistivity of pure Th,  $\rho_L$  is the lattice resistivity,  $\rho_i$  is the temperature-independent resistivity due to the rare-earth impurity, and  $\rho_s$  is the resistivity due to spin-slip scattering. The resistivity due to the Ce only (where the resistivity of pure Th has been subtracted) is plotted versus temperature in Fig. 5. The magnetic impurity scattering is independent of temperature to an accuracy of 0.1%. If the spin-flip scattering has a  $\ln T$  term as described by Kondo, then  $J$  must be much smaller than the nonspin-flip coupling and it must be at least an order of magnitude smaller than the  $J$  values reported by Sugawara.

A negative magnetoresistance often accompanies a resistance minimum so the resistivity of these samples has been measured as a function field  $H$ . All of the samples exhibit a positive magnetoresistance which is approximately linear in  $H^2$ . Figure 6 shows the data for the three samples which most closely obey the  $H^2$  dependence. No clear-cut pattern for the magnitude of the magnetoresistance is apparent but the magnitude of the effect is always small.

#### CONCLUDING REMARKS

The thorium metal which has been prepared by the electrotransport process is probably the most pure reported in the literature. These samples consistently show a resistivity of 15.8  $\mu\Omega$  cm at 300°K. For temperatures above  $\Theta_D$ , there is a rise of the resistivity above the Bloch-Grüneisen law corresponding to the anomaly seen in the specific heat. A rapidly rising density of states at the Fermi energy could cause these effects but other explanations are also possible.

For the thorium-rare-earth alloys there is no resistivity minimum of the type discussed by Kondo and there are no irregularities which might be associated with a Néel temperature.<sup>15,16</sup> This seems to indicate a very weak spin coupling between the impurities and the conduction electrons. To corroborate this conclusion we have measured the depression of the superconducting transition temperature,  $T_c$ , by the addition of Gd. A preliminary measurement gives  $3^\circ\text{K/at.}\%$ , a value much smaller than that found for the transition metals

<sup>15</sup> R. D. Parks and W. A. Little, in *Seventh International Conference on Low Temperature Physics* (University of Toronto Press, Toronto, Canada, 1960).

<sup>16</sup> D. T. Nelson and S. Legvold, *Phys. Rev.* **123**, 80 (1961).

Mn and Cr in Zn,<sup>17</sup> but still comparable to La-Gd.<sup>18</sup> Only the exchange part of the scattering makes a major contribution to the depression of  $T_c$ ,<sup>19</sup> so this result supports the weak-spin-coupling conclusion.

#### ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of J. E. Ostenson in making some of the measurements.

<sup>17</sup> G. Boato, G. Gillinaro, and C. Rizzuto, *Phys. Rev.* **148**, 353 (1966).

<sup>18</sup> B. T. Matthias, H. Suhl, and E. Corenzwit, *J. Phys. Chem. Solids* **13**, 156 (1960).

<sup>19</sup> A. A. Abrikosov and L. P. Gorkov, *Zh. Eksperim. i Teor. Fiz.* **39**, (1960) [English transl.: *Soviet Phys.—JETP* **12**, 1243 (1961)].

### “Muffin-Tin” Potential in Band Calculations\*

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A prescription is given for defining a potential for use in augmented-plane-wave and Green's-function band calculations.

IN the augmented-plane-wave<sup>1</sup> and Green's-function<sup>2</sup> methods for solving the Schrödinger equation in a regular lattice it is usual to divide a cell of the crystal into two regions, one in which the potential is spherically symmetric and the other in which it is constant. This is indicated schematically in Fig. 1 where the two regions are labeled S and R. This “muffin-tin” potential is obtained by assuming a potential  $V(\mathbf{r})$  which has a more complicated spatial form and averaging it, in S over angles and in R over the volume.<sup>3</sup>

We want to suggest here an alternative procedure which seems to us to be particularly appropriate when a self-consistent field band calculation is done.

The starting point is the expression for the total

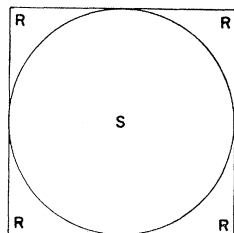


FIG. 1. Schematic diagram of a cell in a crystal lattice. The charge density is assumed to be approximately spherically symmetric in S and approximately constant in R.

energy in the Hartree-Fock approximation:

$$\mathcal{E} = \sum_i \langle i | -\frac{1}{2}\nabla^2 - Z/r | i \rangle + \frac{1}{2} \sum_{ij} [ \langle ij | 1/r_{12} | ij \rangle - \langle ij | 1/r_{12} | ji \rangle ]. \quad (1)$$

(Atomic units are used, and we confine ourselves to a single cell of the crystal with appropriate boundary conditions on the one-electron wave functions.) For the exchange energy we substitute the statistical approximation<sup>4</sup>;

$$-\frac{1}{4\pi^3} \int [3\pi^2 \rho(\mathbf{r})]^{4/3} d\mathbf{r}, \quad (2)$$

where, of course,  $\rho(\mathbf{r}) = \sum_i |\varphi_i(\mathbf{r})|^2$ . In terms of the charge density  $\rho(\mathbf{r})$  the direct part of the potential energy is

$$-Z \int \rho(\mathbf{r})/r d\mathbf{r} + \frac{1}{2} \int \int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| d\mathbf{r} d\mathbf{r}'. \quad (3)$$

The integrals in Eqs. (2) and (3) are now broken up into integrals over the regions R and S. For example,

$$\begin{aligned} \frac{1}{2} \int \int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| d\mathbf{r} d\mathbf{r}' &= \frac{1}{2} \int_{\mathbf{R}} d\mathbf{r} \rho(\mathbf{r}) \int_{\mathbf{R}} d\mathbf{r}' \\ &\times \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| + \int_{\mathbf{R}} d\mathbf{r} \rho(\mathbf{r}) \int_{\mathbf{S}} d\mathbf{r}' \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'| \\ &+ \frac{1}{2} \int_{\mathbf{S}} d\mathbf{r} \rho(\mathbf{r}) \int_{\mathbf{S}} d\mathbf{r}' \rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|. \quad (4) \end{aligned}$$

\* Work performed under the auspices of the U. S. Atomic Commission.

<sup>1</sup> J. C. Slater, *Phys. Rev.* **92**, 603 (1953).

<sup>2</sup> J. Korringa, *Physica* **13**, 392 (1947); W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 1111 (1954); P. M. Morse, *Proc. Natl. Acad. Sci.* **42**, 276 (1956).

<sup>3</sup> F. S. Ham and B. Segall, *Phys. Rev.* **124**, 1786 (1961); P. D. DeCicco, Ph.D. thesis, Massachusetts Institute of Technology, 1962 (unpublished).

<sup>4</sup> R. Gaspar, *Acta Phys. Hung.* **3**, 263 (1954); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).