Electrical Behavior of Plutonium-Neptunium Alloys*

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The electrical behavior of a series of plutonium-neptunium solid-solution alloys has been investigated between 1 and 300°K. The effect of alloying on residual resistivity is substantially different from that usually seen in solid-solution alloys. An interpretation is advanced for this behavior.

INTRODUCTION

PLUTONIUM is one of the few elements which have a large number of allotropic modifications. Plutonium has six in all.[1] In the pure metal the stable form below 395°K is the alpha phase, having a complex monoclinic structure.[2] Experimentally only one element, neptunium, has been found to have appreciable solid solubility in this phase, in contrast to the delta phase of plutonium (fcc), in which many elements are soluble and are able to stabilize the structure to room temperature and below.

The plutonium-neptunium phase diagram, and x-ray lattice constants have been reported by British workers.[3,4] These investigations show that neptunium substitutes nearly ideally, with the 50 at.% neptunium-plutonium alloy showing the crystal structure of pure alpha-phase plutonium and an isotropic shrinkage of lattice parameters of only 1%.

Low-temperature physical measurements of several types have been reported on both polycrystalline and oriented polycrystalline alpha-phase plutonium by a number of authors.[5–10] Low-temperature electrical measurements have been made by King and Lee[11] on beta-phase plutonium. Electrical investigations below room temperature on delta-phase solid-solution alloys have also been reported by a number of authors.[12–14]

The electrical behavior of plutonium is anomalous when compared either to that of normal metals or that of the other actinides. Two theories have been advanced to explain this. The first theory[15] proposes that the electrical anomaly arises from magnetic ordering in plutonium, and is based on the similarity of its electrical behavior to that observed in rare earths, in which magnetic ordering has been demonstrated. The second theory[16] attempts to explain the electrical behavior in terms of a two-band model having overlapping broad and narrow bands.

The investigation described below was undertaken both to compare the electrical behavior of alpha-phase solid-solution alloys with that previously observed for delta-phase alloys, and to elucidate the behavior of plutonium itself.

EXPERIMENTAL

The procedures used in these measurements are described in two previous publications.[9,13] The alloys were prepared by arc-melting together and induction-casting high-purity plutonium metal and suitable amounts of neptunium metal. The chemical composition of the plutonium stock was: plutonium 99.91 wt%; Ta and U each <30 ppm; Fe and Ni each <20 ppm; Th <15 ppm; W 15±5 ppm; Am 15 ppm; Na, Ca, La, Si, Cr, Co, and Zn each <10 ppm; Mg, Mo, and Y each <5 ppm; Pb, Cu, and Mn each <2 ppm; all other impurities less than 2 ppm. (The symbol "less than" indicates that the limit of detection of the analytical method was not exceeded for the element listed.) The neptunium stock used in these alloys had been recovered from trimmings and chips from preparation of an electrical-resistivity rod, and as a consequence contained appreciable amounts of neptunium oxide. Corrections were therefore made for the oxide content of this starting material. Spectrographic analysis of the neptunium showed the following: 0.59 at.% Pu; Th 0.01–0.1 wt%; Na, Ce, Pr, Nd, and Sm each <0.2 wt%; Eu, Ho, Tm, and Lu each <0.1 wt%;

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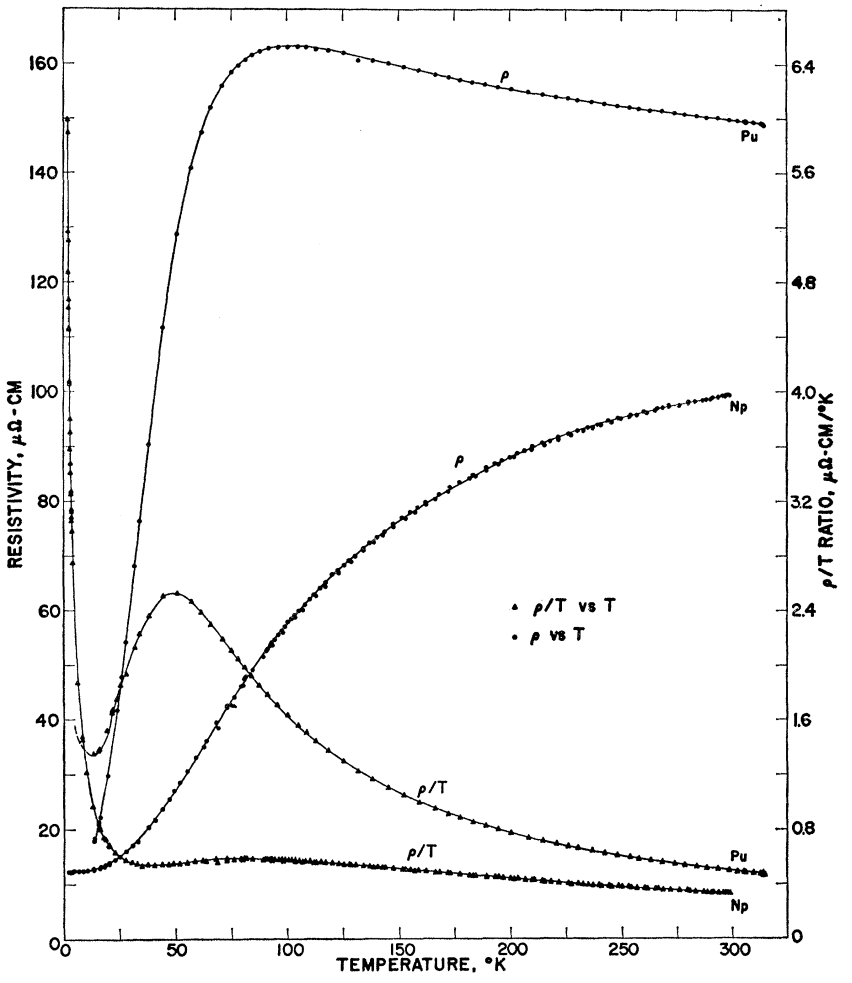

FIG. 1. Resistivity and ρ/T as a function of temperature for the stock plutonium and neptunium.

Al, Se, Ti, Cr, Mn, Fe, Co, Ni, Y, Zr, La, and Yb each <0.05 wt%; Mg, Ca, Sr, and Ba each <0.005 wt%.

EXPERIMENTAL RESULTS

The experimental data are summarized in Figs. 1 through 5 and in Table I. The electrical behaviors of the stock plutonium and neptunium are shown in Fig. 1, as well as plots of ρ/T versus T for these materials. The behavior of the neptunium sample is in qualitative agreement with data reported earlier by Lee *et al.*[17] However, its residual resistivity is higher than that reported by Lee, due probably to higher plutonium content. Further, its room-temperature resistivity is lower than that reported by Lee, indicating that neptunium behaves like plutonium with respect to impurity additions (i.e., impurities which increase the residual resistivity also decrease the room-temperature resistivity).

The experiments were performed in a way to minimize the self-damage in the alloys. Subsequent to this work, several of the alloys were studied for self-damage. This is a subject of another publication, but it can be remarked that the isothermal (20°K) increase in resistivity due to self-damage is qualitatively similar to the resistivity changes produced by increasing temperature in the undamaged material.

Figures 2 and 3 show the temperature variation of resistivity for the alloys which were examined. Figure 4 shows the variation of residual resistivity with composition for selected temperatures, and Fig. 5 the variation of ρ/T versus T with composition. The experimental data are summarized in Table I.

It is apparent that the electrical behavior of alpha plutonium is profoundly modified by neptunium additions. Six at.% of neptunium is sufficient to eliminate all evidence of the low-temperature drop in electrical resistivity typical of unalloyed plutonium. This is to be contrasted with alloying additions to the delta phase, in which even 18 at.% of cerium or 10 at.% of aluminum fail to eliminate the resistivity drop. In addition, the variation of residual resistivity with composition is unusual in that resistivity rises to a maximum in the

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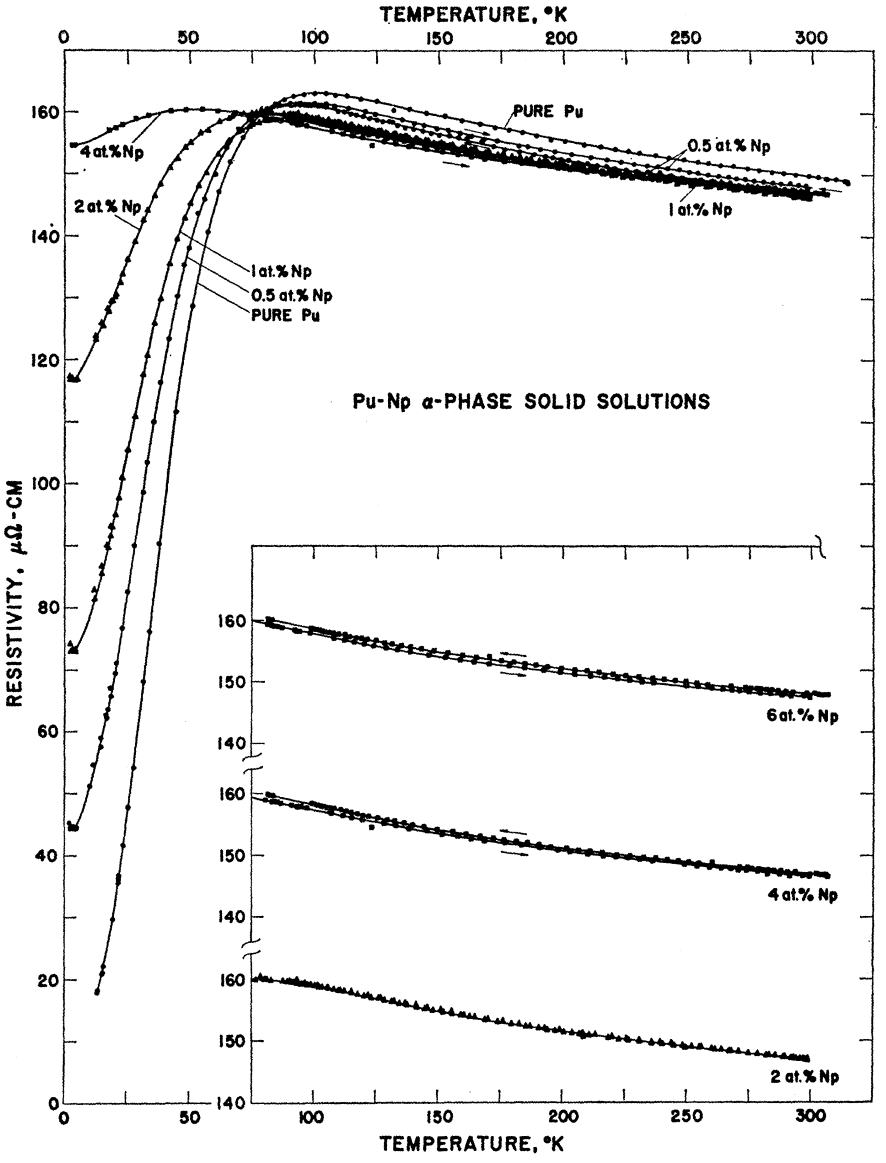

FIG. 2. Resistivity as a function of temperature for several alpha-phase neptunium-plutonium solid-solution alloys.

vicinity of 7 at.% neptunium, falls to a minimum at about 20 at.% neptunium, and then rises again.

While no theoretical basis exists for the minimum observed in the ρ/T versus T plots for alpha-phase plutonoim and neptunium, investigations[9] using such plots have shown that the nature of the minimum depends strongly on the purity of the material and on radiation damage. In the case of uranium such a minimum[18] exists in the ρ/T versus T plot, and this has been found to be associated with the reversal in sign of the expansion in one of the crystallographic directions of uranium. Lallemont[25] reports an expansion minimum in plutonium at 50°K, so that it appears reasonable to postulate that the minimum in the ρ/T versus T plots may be associated with such an anomaly, especially since no anomaly in specific heat or magnetic susceptibility has been found which can be correlated with this minimum.

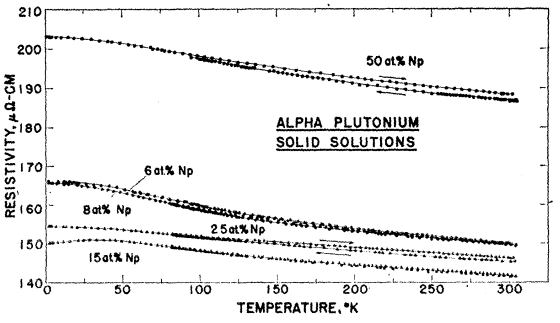

FIG. 3. Resistivity as a function of temperature for several alpha-phase neptunium-plutonium solid-solution alloys.

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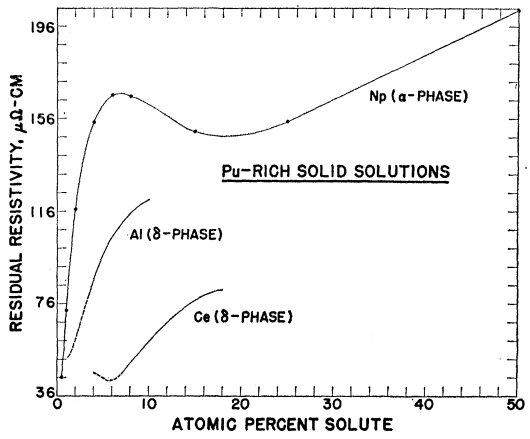

FIG. 4. Comparison of the compositional variation of the alpha-phase neptunium-plutonium solid-solution alloy residual resistivity with that of the alpha-phase aluminum- and cerium-plutonium solid-solution alloys.

DISCUSSION OF RESULTS

The first mechanism postulated for the observed anomaly in the electrical behavior of plutonium was that of magnetic ordering. While this proposal is attractive, especially since intermetallic compounds exhibiting magnetic ordering have been found,[19,20] the preponderance of experimental evidence fails to support it. Specific-heat measurements,[21] Hall-effect measurements,[22,23] neutron-diffraction studies,[24] thermoelectric measurements,[25] and magnetic-susceptibility measurements[26,27] all fail to disclose anomalies which could be associated with a magnetic order-disorder transformation.

The second theory[16] proposes to account for the observed electrical behavior on the basis of a two-band model for the electronic energy states of plutonium. This point of view has been discussed by Lee *et al.*,[12] Smoluchowski,[16] Brodsky,[22] and Meaden,[28] and these references should be consulted for detailed discussions. However, the two-band model encounters difficulty in explaining the reasonably good metallic behavior of plutonium below 100°K.

When a comparison is made of the electrical behavior observed in neptunium-plutonium alloys with that reported for lead-bismuth alloys,[29,30] strong qualitative similarities appear with regard to effects of temperature and alloying additions, even to negative temperature coefficients of resistivity. Note that the temperature-dependent part of the resistivity of neptunium-plutonium alloys varies with increasing neptunium concentration like the temperature-dependent part of the lead-bismuth alloys with decreasing lead concentration. Isothermal plots of Thomson's low-temperature lead-bismuth data plotted as a function of lead concentration show a maximum similar to the one observed in the resistivity of the neptunium-plutonium system. In the lead-bismuth case, the observed behavior has been interpreted[31] as arising from the existence of a Fermi surface at an energy just above that of a prominent Brillouin zone. Lead additions to bismuth are believed to lower the Fermi surface to an energy below that of the zone boundary, producing the observed electrical behavior. The chemical properties[32] of the actinide elements in the series from uranium to curium show that the common chemical valence is reduced from six for uranium to three for curium. This suggests that neptunium may be able to contribute additional electrons to the conduction band of plutonium.

To account for the observed electrical behavior of the neptunium-plutonium alloys, a model[33] similar to bismuth is used in which the Fermi surface of plutonium lies just below prominent Brillouin zone. Neptunium additions which do not disturb the crystal structure significantly add electrons to the conduction band of plutonium. These electron additions appear to fill hole pockets in the first zone, initially causing the conductivity to fall because of impurity scattering and a reduction in the number of carriers. At the maximum in residual resistivity, further neptunium additions in-

TABLE I. Summary of electrical resistivity data for Pu, Np, and α-phase Pu-Np solid-solution alloys.

at.%	Resistivity, μΩ-cm (Residual) 3–4°K	50°K	100°K	300°K	Temp. at ρ_{max} °K	ρ_{max} μΩ-cm
0 (Pure Pu)	···	126.4	163.1	149.7	105	163.1
0.5	44.3	138.8	161.2	147.4	96.1	161.5
1	73.0	145.1	158.8	146.3	90.4	159.1
2	116.9	155.0	159.0	147.0	80.0	160.0
4	154.5	160.4	157.9	146.8	53.0	160.4
6	166.0	164.1	159.9	150.0	···	···
8	165.6	163.2	158.8	149.8	···	···
15	150.3	150.7	148.2	141.8	(35.5)	(151.0)
25	154.6	153.6	151.8	146.0	···	···
50	203.1	201.4	197.8	187.6	···	···
100 (Pure Np)	12.2	27.3	57.3	99.5	···	···

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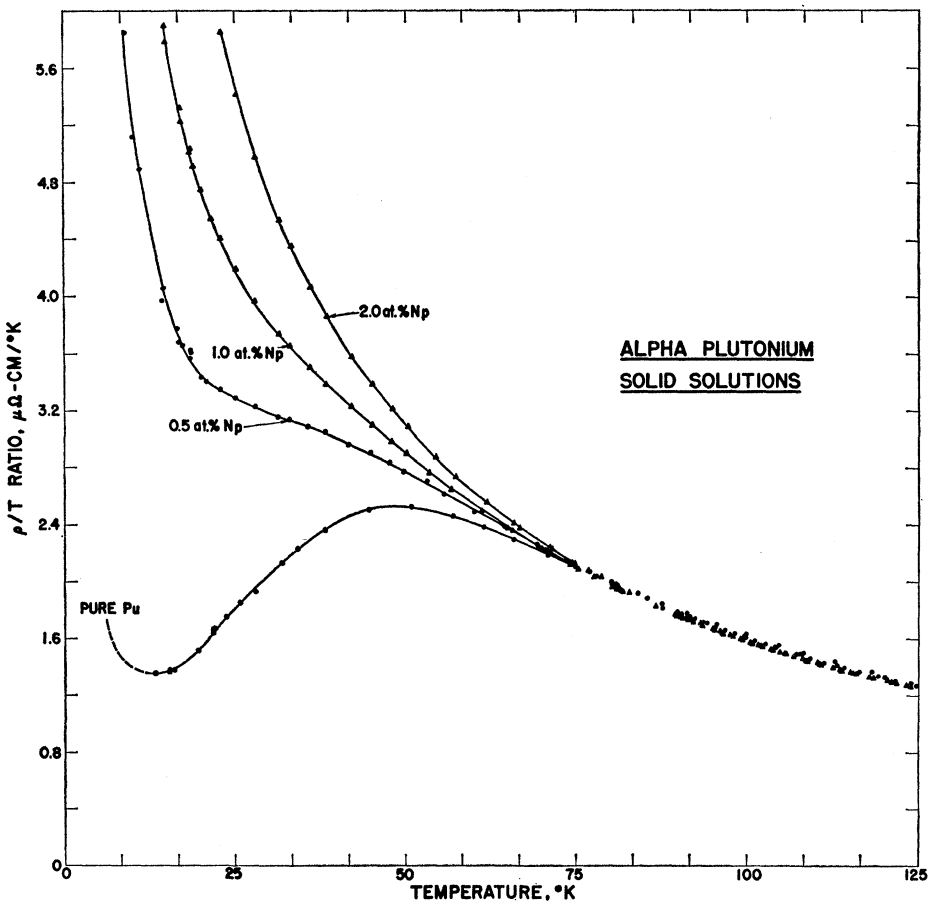

FIG. 5. ρ/T versus temperature behavior of several alpha-phase neptunium-plutonium solid-solution alloys.

crease the carrier concentration by additions to the electron pockets in the second zone so that the conductivity for a composition range increases faster than the monotonically increasing impurity scattering. As a result of the two competing processes, a minimum is produced in the residual electrical resistivity. Further discussions of this model would anticipate a paper by Koenig and Olsen[33] where this model is discussed at length.

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