# Hall Coefficient of Alpha Plutonium*

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The Hall coefficient of alpha plutonium was found to be $+2.8\times10^{-13}$ at 388°K and $-6.5\times10^{-13}$ (V-cm)/(A-G) at 78°K. The variation between these extreme temperatures was found to change gradually with temperature and the value changes sign at 190°K. No field dependence of Hall voltage was found, nor did the application of 11 500 G affect the resistivity maximum at 100°K. It is concluded that the resistivity maximum is not due to magnetic ordering. An observation by Loasby and Taylor that the Hall coefficient changes with time at 77°K was not confirmed here. The results were used to calculate the numbers of holes and electrons as a function of temperature on the two-band model. The calculations show that a narrow 5*f*-6*d* band and broad 7*s* conduction band is more likely than a narrow 5*f* and broad 6*d* band.

## INTRODUCTION

ATTEMPTS have been made to explain the anomalous properties of plutonium on the basis of a two-band model.[1–6] It was concluded that there is a broad 6*d* conduction band and a narrow 5*f* band, both of which overlap the Fermi surface. This is similar to Friedel's[7] model for uranium except that Friedel has proposed a 7*s* conduction band and a mixed 5*f*-6*d* narrow band. One of the anomalous properties is the electrical resistivity maximum at 100°K in monoclinic alpha plutonium. This has been discussed at great length elsewhere[5–9] and is thought to be due to interband scattering[5,6] or to magnetic order-disorder.[8–10]

This investigation of the Hall coefficient of pure alpha Pu was undertaken to determine the applicability of the two-band model to plutonium and to observe what effects would be found at the temperature of the resistivity maximum, especially since Loasby and Taylor[11] found different signs for the Hall coefficient at 77 and 293°K. Measurements were made between 78 and 388°K on high purity, polycrystalline rolled sheet. The Hall coefficient was determined as a function of applied field at five temperatures, including one set of measurements in the range of the resistivity hump. Data were also taken at 78 and 88°K as a function of time to check the assertion[11] that the Hall coefficient varies with time at 77°K. The results are discussed in terms of proposed band structures of plutonium.

## EXPERIMENTAL

A standard, four-probe, dc method was used, in which sample current densities of about 35 A/cm² were produced by a bank of storage batteries. Voltages were read on a Keithley dc millimicrovoltmeter usually to a precision of one part in one hundred. The voltage leads were made equipotential at zero field by means of the buck-out circuit on the instrument. Leads were attached to the sample by soft-solder and the assembly was taped to a Lucite backing and inserted into a tight fitting copper container. A calibrated copper-constantan thermocouple was pressed against the center of the sample and held in place by the tape. The copper can was connected to a nitrogen-filled glovebox[12] by means of plastic and stainless steel tubing at all times to eliminate the need for sealing off the assembly from the glovebox.

Measurements were made with a two-inch, iron-core electromagnet, which produced fields of 5200 G at $\frac{7}{16}$ in. and 11 500 G at $\frac{3}{16}$ in., the two gap-widths which were used. The results were averaged for four sets of readings, i. e., with the current and field in each of two directions.

Temperatures above 298°K were obtained with resistance wire wound around the sample container. Temperatures between room temperature and 83°K were achieved by passing precooled nitrogen gas through copper tubes soldered to the edges of the sample can. Measurements were made at 78°K by inserting the sample assembly in an insulated container of liquid nitrogen which fit into the $\frac{7}{16}$-in. gap. Data above 83° were obtained in the $\frac{3}{16}$-in. gap.

Samples were made from electrolytic, high-purity metal.[13] The analysis of the metal, in parts per million by weight, was: C-6; H-3.1; O-10; N-10; U-26; Si-6; Al-10; Cr-8; Fe-15; Ga-4; K-20; Li-0.1; Mn-0.5; Mo-2; and Ni-10. Other elements were below the levels of detection. The americium content, due to decay of $Pu^{241}$, was about 80 ppm at the time of measurements. Sheet specimens were made by cross-rolling in the beta phase

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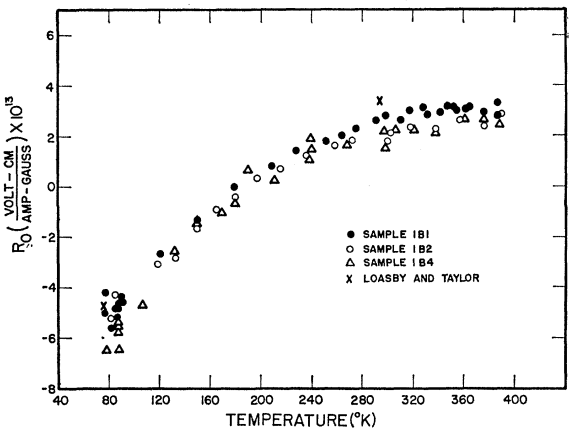


FIG. 1. Hall coefficient of alpha plutonium.

to 0.03 cm thick and then rolling in the alpha phase to straighten the piece and to reduce it to about 0.025 cm thick.

## RESULTS AND DISCUSSION

### Temperature Behavior and the Resistivity Maximum

Figure 1 shows the Hall coefficient of alpha Pu as a function of temperature for three samples. It is seen that Loasby and Taylor's[11] observation that the coefficient changes sign between 77 and 293°K is verified and, surprisingly, the change is gradual.[13a] There is no indication of a sudden change at 100°K, the temperature of the resistivity maximum, although the data scatter reduces the certainty of this observation.

Since alpha Pu is monoclinic, data obtained from polycrystalline samples could exhibit preferred orientation effects. Because of this, sample 1*B*4 was cut perpendicular to samples 1*B*1 and 1*B*2, and it is seen that the three samples give nearly the same results. In fact, the data from samples 1*B*2 and 1*B*4 are almost identical. Some of the differences may have been due to misalignment which occurred during sample changes or gap adjustments.

The existence of an antiferromagnetic state in plutonium at 100°K has been postulated due to the similarities in the resistivity–temperature curves of Pu, Dy, Tb, and alpha Mn.[8–10] Should this be so, the Hall voltage of alpha-Pu should vary nonlinearly with applied field[14] and probably exhibit anomalous behavior near the temperature of the paramagnetic–antiferromagnetic transition.[15] Measurements of the Hall voltage were made as a function of applied field at 88, 107, 167, 240, and 306°K. In each case, no effect of field on the slope of the curve was observed. Furthermore, the change in sign of $R_0$ occurs near 190°K, well away from the temperature of the resistivity maximum.

As a further check on the possible existence of magnetic ordering near 100°K, the resistivity of a sample, 1*B*5, was measured between 88 and 295°K with and without a transverse magnetic field of 11 500 G. The sample showed the usual resistivity maximum, at about 110°K in this case, in the absence of the field. There was no observable change in resistivity, to one part in five thousand, with the application of the field. This result may be compared to terbium, for example, in which 11 350 G caused a drop in the resistivity maximum of 4%.[16] If the usual increase of resistivity with magnetic field is about the same for plutonium as for thorium and uranium,[17] one would expect an increase due to "normal" magnetoresistivity of about one part in $10^4$, which should have no effect on the expected decrease for antiferromagnetic disordering. Thus, it would seem that antiferromagnetic ordering is not responsible for the resistivity maximum; it might be due to interband scattering.[5]

### Change in $R_0$ with Time

Loasby and Taylor[11] reported that $R_0$ at 77°K was a function of time and doubled in 6 h. This effect was thought to be related to the cycling effects found in specific-heat measurements,[18,19] which are in turn likely due to self-radiation damage.[19] This behavior of $R_0$ was checked at 78 and 88°K and the data are given in Fig.

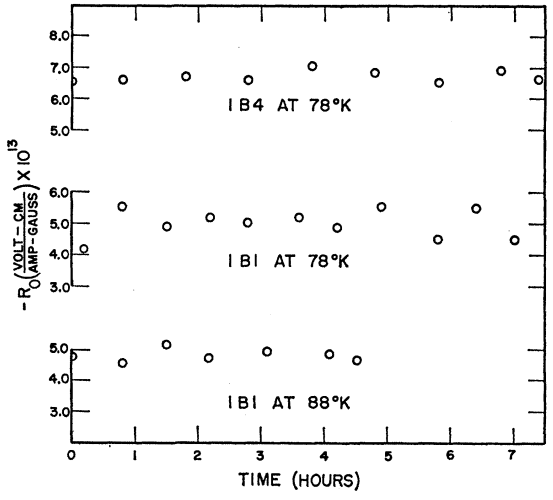


FIG. 2. Change in Hall coefficient with time.

[13a] *Note added in proof.* It has been pointed out by R. G. Loasby (private communication) that the data from Ref. 11 have been given erroneously in Fig. 1. The correct values from Loasby and Taylor are $+6.9\times10^{-13}$ (V-cm)/(A-G) at 293°K and $-9.5\times10^{-13}$ (V-cm)/(A-G) at 77°K.

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2. It is seen that there is no effect of time at these temperatures.

An effect of the order observed in the earlier work[11] would be quite large if due to self-radiation damage. Alpha Pu damages at a rate of $1.2\times10^{-3}$ to $1.7\times10^{-3}$ $\mu\Omega$ cm/h at 77°K.[20] This has been verified on metal of similar purity to that used in this work (unpublished data) and represents a change of only one part in $10^4$ in 6 h. If it is assumed that the effect of radiation damage on the Hall coefficient can be estimated by the change in electron mobility corresponding to the increase in resistivity, an increase of a factor of 2 in $R_0$ is much too large. A more likely explanation of the observed change in $R_0$ may lie in the time necessary to achieve thermal equilibrium at 77°K. The Hall coefficient seems to double over a range of about 30°K near 77°K and long times could be necessary for true equilibration under some experimental conditions.

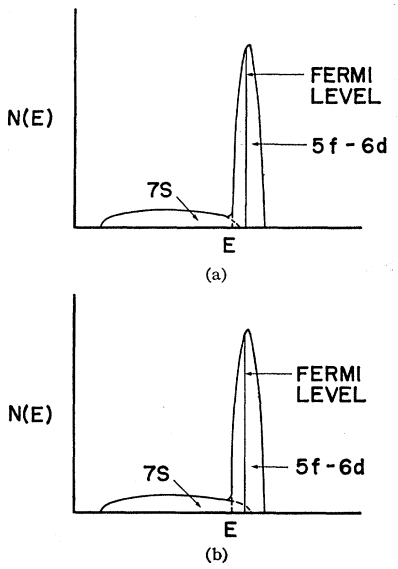


FIG. 4. Proposed band overlap (schematic) with increasing temperature for plutonium; (a)below 190°K, (b) above 190°K.

### The Band Structure of Plutonium

The two-band model of conduction has been successfully applied to the rare earths and leads to the following result[15]:

$$R_0=\frac{1}{Ne}\frac{n_h-n_e\mu_e^2/\mu_h^2}{(n_h+n_e\mu_e/\mu_h)^2},$$

where $R_0$ is the ordinary Hall coefficient, $N$ the number of atoms per unit volume, $e$ the magnitude of the electronic charge, $n_h$ the number of electron holes per atom in the nearly full band, and $n_e$ the number of electrons per atom in the nearly empty band; $\mu_e$ and $\mu_h$ are the respective mobilities of the electrons and holes.

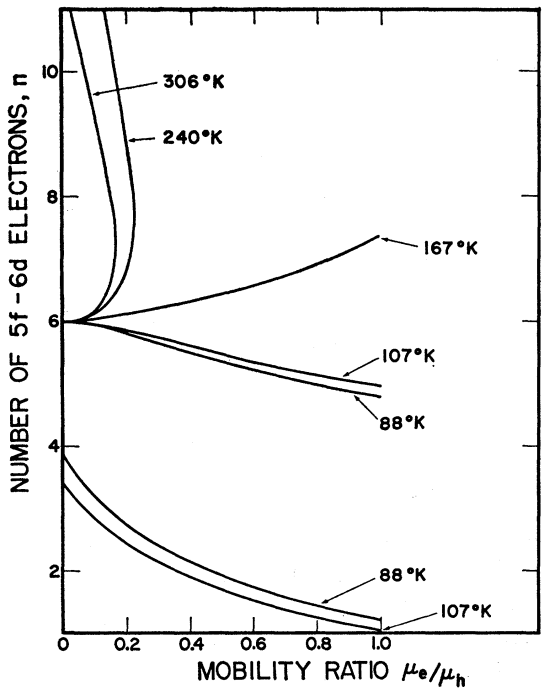


FIG. 3. Calculated number of electrons in narrow 5*f*–6*d* band at various temperatures.

The two models to be considered are a broad 6*d* with a narrow 5*f* band[2–4] and a broad 7*s* band with a narrow hybrid 5*f*-6*d* band.[7] In the former case, the eight electrons are distributed to nearly fill the 6*d* band causing electron holes and any electrons in the 5*f* band exist as electrons. An expression between $n_h$ and $n_e$ can then be obtained, $n_h=n_e+2$. In the case of the nearly full 7*s* band, the relation becomes $n_h=n_e-6$. Since the electron conduction bands, 5*f* or 5*f*-6*d* hybrid, are much more narrow than the respective broad band,[2–7] solutions of interest should lie below $\mu_e/\mu_h=1.0$.

The above expression for the two-band model has been solved for the two assumed band pictures. Solutions for a 5*d* conduction band are negative or imaginary for the temperatures at which $R_0$ is negative. Solutions at the higher two temperatures are also unrealistic, yielding electron populations in the 5*d* band much too low to permit hole conduction. The results for the 7*s* conduction band are, conversely, real and positive. These results for a 7*s* conduction band are shown in Fig. 3 at five temperatures. Calculated values at $\mu_e/\mu_h=0.05$, for example, yield $n_h=0.04$, 0.03, 0.01, −0.01, and −0.02, with decreasing temperature when the lower branch of the solution is used. Uncertainties in the $R_0$'s and in the density[21] may be responsible for the slight negative values for $n_h$.

Despite the uncertainties in the calculation, a consistent picture may be obtained utilizing a 7*s* conduction band, but not with a 6*d* conduction band. At the lower temperatures, the Fermi level is at a higher level than the top of the 7*s* band and the 7*s* band is full. As the temperature is increased, the top of the 7*s* band

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broadens, due to thermal excitation, faster than the increase of the Fermi level, until the Fermi level is below the band top and holes are formed in the 7*s* band leading to a positive Hall coefficient. This is shown schematically in Fig. 4.

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# Superconductivity at High Magnetic Fields*

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Using pulsed-magnetic-field techniques, we have studied the magnetic-field-induced superconducting transitions of alloys in the systems Ti-V, Ti-Nb, Ti-Ta, Ti-Mo, Zr-Nb, Hf-Nb, Hf-Ta, U-Nb, and U-Mo. For concentrated alloys the low-current-density resistive critical field $H_r(J \lesssim 10\ \mathrm{A/cm^2})$ is nearly independent of the amount of cold working and the relative orientations of magnetic field, current, and anisotropic defect structure. The observed values of $H_r(J=10)$ peak up sharply (reaching 145 kG in the Ti-Nb system) in the vicinity of ~4.5 "valence" electrons per atom, an electron concentration where peaking also typically occurs for such (approximately) defect-independent transition metal alloy parameters as superconducting transition temperature, thermodynamic critical field, and electronic specific heat coefficient. All the above evidence suggests that in these alloys $H_r(J=10)$ is determined principally by bulk electronic parameters, rather than by the nature of extended lattice defects. This view is further supported by the observation that, for several Group V-rich, Group IV–Group V transition metal alloys, excellent quantitative agreement is achieved in adjustable-parameter-free comparisons of $H_r(J=10)$ with $H_{c2}$, the "upper critical field" predicted on the basis of bulk electronic parameters by the Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory for the case of negative surface energy. For certain ranges of alloy composition, it appears that normal-state paramagnetic free-energy considerations, ignored in the GLAG theory, impose limitations on $H_r(J=10)$ in good accord with the theoretical predictions of Clogston. Additional experimental results are reviewed, and it is argued that a comprehensive theoretical understanding of high-field superconductivity in bulk materials may be achieved on the basis of the GLAG theory, modified to include paramagnetic free-energy terms, and extended to consider transport supercurrents stabilized in a manner similar to that suggested by Gorter and Anderson. The *a priori* assumptions of Mendelssohn's filamentary-mesh model appear, on the other hand, to be inadequate for a suitable description.

## I. INTRODUCTION

RECENT progress in the understanding and characterization of high-magnetic-field superconductors has been particularly rapid, and the broad outlines of a reasonable picture appear already to have been established. Significant differences exist between this picture and the earliest model. The latter, hereafter referred to as the filamentary-mesh model, hypothesized a multiply connected high-critical-field filamentary network embedded in a matrix of low-critical-field material.[1] The high critical fields of the filaments followed either from chemical or physical inhomogeneity[1] directly or (on simple thermodynamic arguments) from the small filament dimensions,[2–5] i.e., any observed filamentary critical field could be rationalized by the assumption of a suitable filament diameter. Such ideas have recently been widely assumed to account satisfactorily for most properties of high-magnetic-field superconductors.[3–7] However, for reasons to be discussed at length below, an alternative (and more general) interpretation of high-field superconductivity is gaining wide acceptance. In this alternative picture, the main bulk of a high-field superconductor remains superconducting up to an "upper critical field" determined by bulk (or nonfilamentary) electronic parameters, essentially as predicted by the "homogeneous" Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory.[8–11] In certain cases,[12] the upper critical field may be limited as predicted by Clogston[13]

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