PROPERTIES OF TRANSURANIC METALS

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A report is given on the properties of the actinide metals covering both equilibrium properties and the changes observed as the result of self-irradiation. Anomalies in the resistivity become more pronounced with rising atomic number and reach a very striking appearance in the case of plutonium. Small anomalies have also been found in the specific heat of uranium and plutonim. A short account is given of the methods of investigation and the conclusion is reached that the anomalous behaviour is due to some form of magnetic ordering.

Preface

About thirty-five years ago Dr. Niewodniczański, who at that time was Docent at the University of Vilno, had obtained a Rockefeller grant for carrying out research at Cambridge. He was given working facilities at the new Royal Society Mond Laboratory and, using liquid helium from the machine designed there by Kapitza, he embarked, together with Henry Boorse, on an investigation of the resistivity of aluminium. Shortly after his arrival he came over to Oxford where, at the Clarendon Laboratory I had set up a small helium plant. It was on this visit that we first met. Working in the same field, we soon became friends, and this friendship continued after his departure from England. I was happy to learn after the war that he had survived and in the following years we often met again during his visits to England or at scientific congresses. With particular pleasure I recall a visit to Cracow when he showed me not only his laboratory but also the ancient University where Copernicus had studied and the laboratories of Wroblewski and Olszewski. We also went to the new Nuclear Physic Institute, a field to which his interest had shifted. It is therefore fitting that this paper, dedicated to the memory of Professor Niewodniczański should deal with both low temperatures and nuclear physics.

Introduction

Pre-war versions of the periodic table of elements still show the heavy metals beyond actinium in the succesive columns, ending with uranium standing below tungsten in column VIa. It was only after transuranic elements had been produced artificially that their signi-

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ficance as a series with unfilled lower *f*-shells was fully appreciated. They thus correspond in many respects to the rare earth metals following lanthanum and it was to be expected that, like the latter, they might exhibit a number of anomalous properties. As the example of the rare earths had shown, these phenomena are likely to become apparent at low temperatures only and a systematic study of the actinides in this region was therefore indicated. This work had to wait until these elements had become available in metallic form and in sufficient quantity and purity. Even then their investigation presented unusual problems due to their extreme radioactive toxicity and the self heat attending their decay. It was clear that the resources of the conventional university laboratory would prove quite inadequate and we therefore initiated a joint research programme of the Physics Department of Oxford University and the Atomic Energy Research Establishment at Harwell.

This project has now been in operation for ten years and the present paper gives an account of the results obtained so far. As will be seen, a large body of data has been assembled and we now have a fair knowledge of the physical properties of these metals. On the other hand, we also have found a number of quite unexpected and puzzling phenomena which so far have defied all attempts at explanation and it is clear that much further research is required before we will be able to give an adequate interpretation of the behaviour of the actinides.

Our work has covered the series from thorium to plutonium, americium being as yet available in very small amounts only and introducing additional difficulties by its high gamma-activity. Curium, if it becomes available as a metal will probably be incandescent owing to its high self heat. Metallic protoactinium has become available only quite recently in small amounts and of doubtful purity but such data as we have gathered so far fit in reasonably well with our knowledge of the other actinides. Our main effort has been concentrated on plutonium which, apart from being technologically important, has exhibited the most interesting properties of the whole series.

Departing from the historical sequence of the experiments, the present account will be divided into a report on the equilibrium properties of the metals, to be followed by a description of the effects produced by the accumulation of radiation damage when the metal is held at low temperatures and finally the information which the latter results have on the general physical aspects will be discussed. These accounts are preceded by a short description of the methods used.

Experimental methods

For the first experiments a cryostat was constructed the top of which opened out into an active glove box while the low temperature section protruded below the latter. This was outside the active area except for the inside of a central tube. Measurements on resistivity and thermo emf. could be carried out on samples which had been prepared in the glove box and then inserted into this tube.

When it became apparent that, in order to study the effect of radiation damage, resistivity experiments in liquid helium had to be extended to periods of the order of 20.000 hours, the technique had to be changed. Specimens were sealed into cylindrical capsules filled

with helium gas and with the leads carried out through a long steel tube. These capsules were inserted through the neck into standard 18 litre helium storage vessels, a single filling of which lasted for about 500 hrs.

A special cryostat was designed for the specific heat measurements which were carried out on samples sealed hermetically into metal calorimeters. In view of the high self heat in the case of plutonium, this heat was used as a constant source. In order to avoid heat losses or gains which might falsify the results, the calorimeter was surrounded by an electronically monitored adiabatic shield.

Equilibrium properties

The resistivities of the actinide metals show a gradual departure from the normal pattern with increasing atomic number. The first traces of concavity towards the temperature axis appear in uranium and this is much enhanced in neptunium. α-plutonium is highly anomalous with a rapid rise from helium temperatures to a flat maximum in the neighbourhood of 100°K which is followed by a negative temperature coefficient that is maintained up to 112°C where the monoclinic α-phase transforms into the body-centred monoclinic β-phase. It has been possible to investigate this latter phase, too, by quenching it from high temperatures into liquid nitrogen where transformation into the stable α-phase is slow enough to permit experiments. Finally, the δ-phase which is face-centred cubic and stable between 320 and 450°C was measured after it had been stabilized by adding small percentages of aluminium. Both the β and the δ-phases show a maximum in the resistivity. In the former case this is much sharper than in the α-phase and occurs at about 25°K; the position of the maximum in the δ-phase depends on the concentration of the second constituent. Extrapolation suggests a flat maximum between 100 and 150°K for the pure δ-phase.

The temperature coefficient of the resistivity at the lowest temperatures is for all metals roughly the same with a power index of 3, it seems to be somewhat lower for α-plutonium where the resistance rises approximately as $T^{2.3}$. However, the determination of the ideal resistance is not very accurate and these figures can only serve as a rough guide. The temperature dependence of the resistance of β-plutonium at the lowest temperature is greater than of any other metal, being of the order of 3 $\mu\Omega$ cm deg^{-1} at 1.7°K. At temperatures of this order neither neptunium nor plutonium showed superconductivity and we also have failed to observe this effect in our sample of protoactinium.

Apart from early measurements of the specific heat of α-plutonium carried out at Los Alamos which yielded very erratic results, more recent work on this metal as well as on uranium and thorium have indicated no anomalies. Using the very sensitive method mentioned above, we have measured the specific heats of neptunium, α-plutonium and recently also of α-uranium. All these metals have a very high electronic specific heat which in the case of plutonium amounts to 3×10^{-3}cal mol^{-1} deg^{-2}T. The Debye characteristic temperature of this metal is of the order of 160. Whereas no anomaly was detected in neptunium, small but distinct deviations from the smooth function were detected in plutonium and uranium at 60°K and 43°K respectively. The energies involved are quite small, 0.05 RT

in plutonium and 0.09 RT in uranium. Subtracting from our measured data a smooth specific heat function, the anomalies appear as peaks characteristic of second order transformations and, in view of their small size they might be compared with the slightly larger ones observed in chromium and α-manganese which are connected with magnetic ordering.

Our detailed measurements of the resistivity of α-uranium in this temperature region have revealed a slight kink in the smooth function at 43°K. Since in the corresponding temperature region the resistivity of plutonium varies rapidly, the existing data do not permit a decision on whether a similar effect exists in that metal.

Radiation damage effects

It was noted in our early resistivity experiments on plutonium at helium temperatures that the observed values seemed to be rising slightly in the course of measurement. Further work then showed clearly that damage due to the own alpha activity of the substance is accumulated at these temperatures. This effect and its attendant features has claimed a major share of our attention and a thorough investigation, involving experiments of very long duration (up to 20.000 hrs and more), has yielded a fairly clear picture of the general pattern. In the present account the main features of the effect are given, leaving out all detail and a number of ancillary investigations, as for instance the data on annealing.

At helium temperatures the resistivity of α-plutonium rises initially by about 0.6 $\mu\Omega$cm per hour. This rate of rise decreases with accumulating damage, coming close to saturation after between 5.000 and 10.000 hours and depending on the isotopic content of the individual sample. Leaving out secondary features, such as a reversal in rise coefficient at the beginning and the tendency to exhibit a very flat maximum at saturation, the resistivity can be represented in first approximation as

$$r = r_0 + (r_\infty - r_0)(1 - e^{-at}),$$

where r_0 is the initial value and r_∞ that at saturation; t is the time and a is a constant proportional to the self heat of the sample.

Similar effects have been found in ^{231}Pa, ^{233}U, ^{237}Np as well as in β-plutonium. In the latter case the initial rise is about twice as fast as in the α-phase while in the other metals it is much slower. The resistivity of δ-plutonium, too, rises with time but here the rate depends on the concentration of the stabilizing metal and is generally lower than for the other modifications.

Since no appreciable annealing takes place in α-plutonium until about 40°K, it was possible to determine the temperature dependence of the resistivity up to this temperature under varying degrees of selfdamage. Moreover, by changing the specimen temperature rapidly, some values could be obtained to almost 100°K. After accumulating damage for some time, the resistance-temperature curve is found to be flattened out and while at low temperatures the resistance has increased much, the rise is smaller at higher temperatures. In fact at about 60°K the resistance curve of the irradiated sample crosses that of the undamaged specimen. Above this temperature we have the strange situation that the resistance of damaged plutonium is lower than that of the metal in its undamaged state.

These results show that for damaged α-plutonium Matthiesen's rule is not obeyed, *i.e.* the additional resistance is not temperature independent. This effect has been investigated in some detail not only in the α-phase but also in the β and δ-phases where the same effect was found to occur. We are not inclined to ascribe this strange phenomenon to the particular

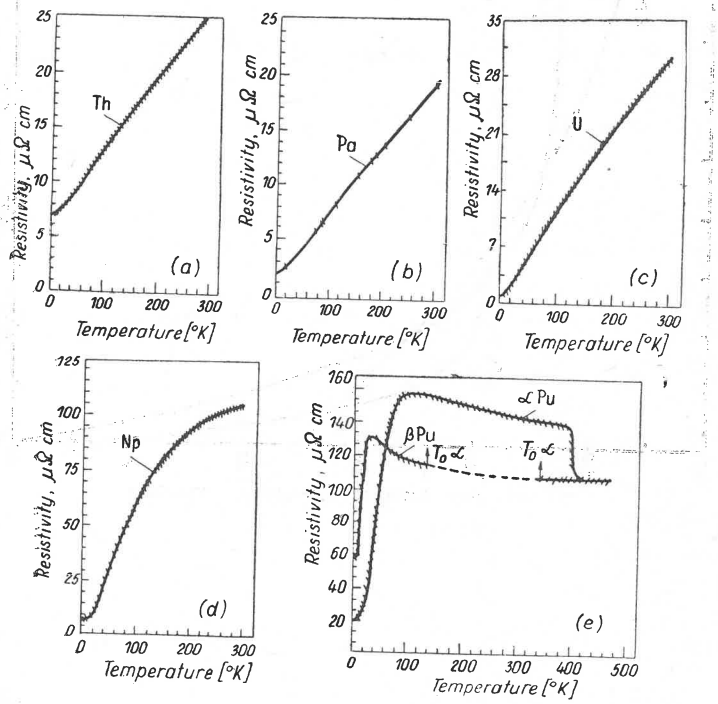

Fig. 1. Temperature dependence of the electrical resistivity of thorium, protoactinium, uranium, neptunium and plutonium

nature of the damage produced by self-irradiation but rather to the nature of the scattering process that causes the unusually high and strongly temperature dependent resistivity in the undamaged metal. It appears, in fact that this scattering mechanism is profoundly influenced by radiation damage.

In order to investigate further the nature of this effect we have carried out measurements on α-manganese, the only substance having a resistivity whose temperature dependence resembles that of plutonium and which is also known to be anti-ferromagnetic. A sample of this metal was subjected at 30°K to irradiation in doses of the order of 10^7 protons cm^{-2} and its resistance was measured at various stages of the treatment, which included annealing, between 4° and 150°K. In this way a series of resistance-temperature curves for varying degree of damage were established. Their character shows a striking similarity with those obtained on the plutonium samples after self damage. In particular, the manganese curves, too, fail to obey Matthiesen's rule.

Finally we have made measurements of the specific heat of α-plutonium on samples which had been kept at about 10°K for 15 and 30 hours. The results show quite clearly the

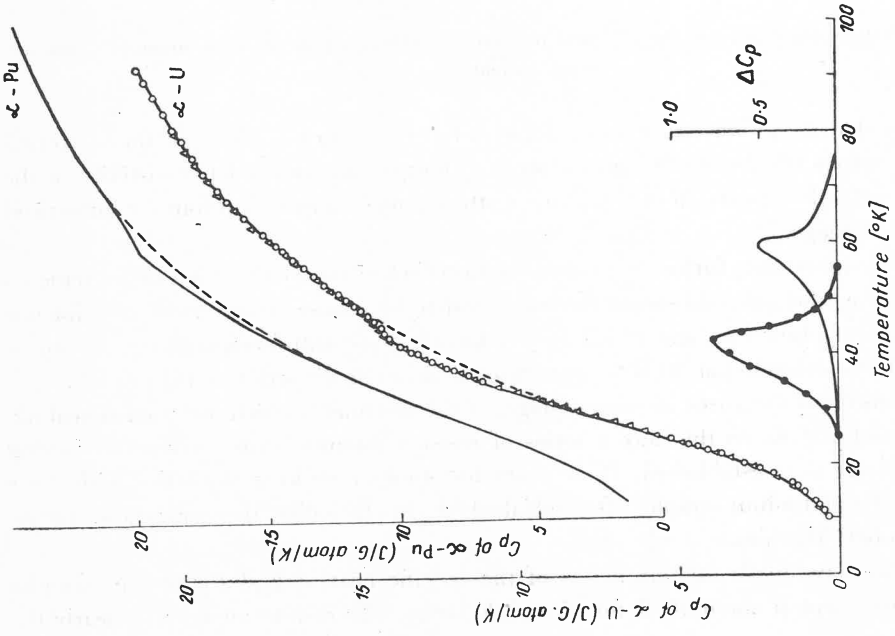

Fig. 2

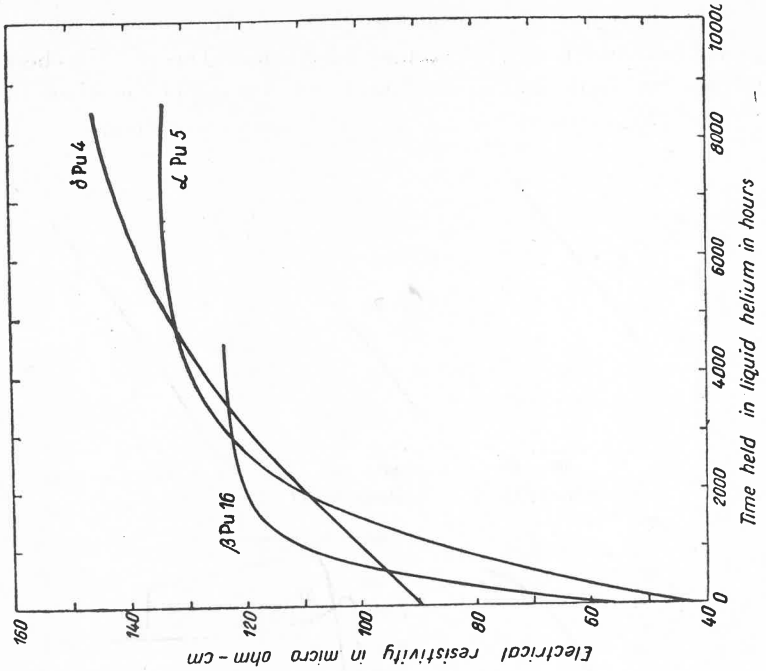

Fig. 3

Fig. 2. Specific heats (C_p) of uranium and plutonium between 10° and 90°K and the anomalies determined as difference between measured and smoothed values
Fig. 3. Resistivities of α-, β-, and δ-plutonium as a function of time at ~5°K

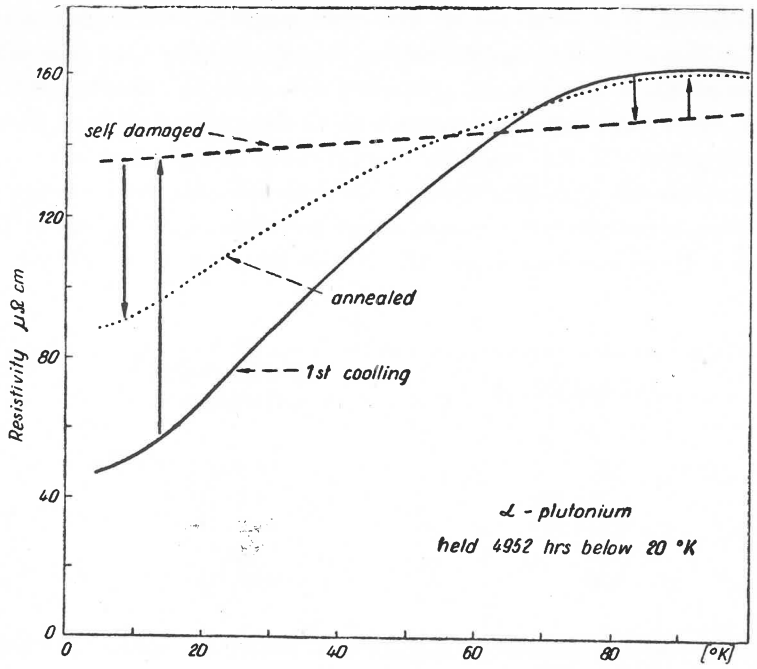

Fig. 4. Resistivity — temperature function of α-plutonium on first cooling (full curve), after holding below 20°K for 4952 hours (broken curve) and after partial annealing (dotted curve)

release of the stored damage energy which sets in at about 50°K and rises to a maximum in the neighbourhood of 80°K, in good agreement with our observations on the resistivity changes in damaged samples. It is, unfortunately not possible to decide whether or not the small anomaly in the specific heat at 60°K is influenced by damage since the effect is overshadowed by the beginning of the energy release.

Conclusions

The two most striking features which our work has brought to light are the anomalous behaviour of the resistivity which becomes more pronounced with increasing atomic number and the specific heat anomalies in uranium and plutonium. It is at present impossible to say whether there is any connexion between these phenomena. The absence of such an anomaly in the specific heat of neptunium may not be significant since its appearance seems to be strongly influenced by the degree of purity. It should, in any case, be kept in mind that in these heavy metals chemical and physical impurity present considerable problems.

A number of suggestions have been made to explain the behaviour of plutonium on the basis of a band model, however, our observation of essentially the same resistive pattern in three different crystal modifications of the metal does not encourage this approach. In spite of the absence of any striking effect in the magnetic susceptibility, we have always been inclined to regard the anomalous behaviour of the heavier actinides as due to some form

of magnetic ordering. It is worth noting that often magnetic co-operative states, such as in manganese or chromium show no anomaly in the susceptibility. The resemblance of the specific heat anomalies in uranium and plutonium with those in chromium and manganese is encouraging. Even more significant appears to us the unusual effect of damage on the temperature dependence of the resistivity in plutonium and manganese.

A clear indication that with rising atomic number the same unusual scattering mechanism gradually develops is provided by a comparison of the effect of self damage in these metals shown in Table I. It can be seen that, in spite of wide variations in the activity, as given by

TABLE I

Metal	Self-heat (mW/g)	Resistivity rise/Self-heat ($\mu\Omega$ cm/h)/(mW/g)
^{231}Pa	1.21	0.826×10^{-3}
^{233}U	2.75×10^{-1}	2.86×10^{-3}
^{237}NP	1.97×10^{-2}	10.9×10^{-3}
α-^{239}Pu	2.50	24.0×10^{-3}
β-^{239}Pu	2.50	40.0×10^{-3}

the self heat, the relevant quantity, resistivity rise divided by self-heat, is rising steadily from protoactinium to β-plutonium.

The names of those who have taken part in this research appear in the bibliography below. They are too numerous to be mentioned individually, except for my colleague, Dr J. A. Lee, the leader of the team at AERE Harwell whose knowledge of the properties of the transuranic metals and of the methods of handling them has guided us all throughout this work.

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