LOW TEMPERATURE PROPERTIES OF TRANSURANIC AND OTHER HEAVY METALS

A study of the effects of self-irradiation damage on the electrical resistivity of alpha and delta stabilised plutonium, uranium and neptunium

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ABSTRACT

The transuranic metals, neptunium and plutonium, are strong alpha emitters and have to be handled under special conditions to safeguard the health of those working with them. The most common method of containing these metals is to use glove boxes but in certain circumstances it is possible to encapsulate specimens for experimental purposes. The relative merits of the use of glove boxes and sealed capsules for cryogenic experiments are discussed in this thesis.

A further consequence of the high alpha activity of these metals is their property of self heating. This self heat is a result of the absorption by the crystal lattice of the kinetic energies of the alpha particle and the recoil nucleus. At room temperature this has little or no effect on the physical properties of these metals, but at low temperatures it is possible for the defects produced in the lattice to remain in equilibrium with their surroundings.

The resistivities of alpha and delta stabilised plutonium, neptunium and uranium 233 are found to increase when these metals are held at low temperatures for long periods of time. Little work on the self-irradiation of uranium 233 and neptunium has been undertaken because of their low self heats and the consequent long self-irradiation times necessary to cause a significant increase in their low temperature resistivities. The storage and annealing of defects in alpha and delta stabilised plutonium have however been studied in considerable detail.

The resistivity of alpha plutonium has an extremely anomalous

temperature dependence. As the temperature falls from room temperature the resistivity first rises slowly to a maximum at ~ 105°K, then drops sharply as the temperature is further lowered to zero. Its residual resistivity is high and very sensitive to small impurity concentrations. It is found that over a period of about 5,000 hours at ~ 5°K the resistivity of alpha plutonium increases from between ~ 20 and ~ 50 $\mu\Omega$ cm. to approximately 140 - 145 $\mu\Omega$cm. ; Some 15 - 20 $\mu\Omega$cm. lower than the value of the resistivity maximum at ~ 105°K. Furthermore the additional resistivity caused by self-irradiation at ~ 5°K does not obey Matthiessen's rule and it is found that after long periods of self-irradiation at ~ 5°K the resistivity measured at ~ 77°K has decreased by about 15 - 20 $\mu\Omega$cm. More detailed investigation of the increase in resistivity during self-irradiation at ~ 5°K shows that the additional resistivity decreases steadily with increase in temperature, becoming zero at ~ 55°K and then negative above ~ 55°K. In contrast, self-irradiation at ~ 77°K causes an increase in the resistivity both at ~ 5°K and ~ 77°K.

The resistivity of delta stabilised plutonium also increases when held at low temperatures for long periods of time. The initial rate of resistivity increase is however much lower than that of alpha plutonium and is found to be dependent on the concentration of aluminium used to stabilise the delta phase. Although the resistivity of delta stabilised plutonium increases initially at a lower rate than alpha plutonium it does not saturate so quickly and eventually rises to values considerably in excess of that of its original resistivity maximum.

The additional resistivity produced in alpha plutonium is found to anneal in two distinct stages. The first stage is centred about 80°K and analysis shows that the activation energy of the recovery process is approximately 0.2 eV. At 90°K the anneal is found to be characterised by second order reaction kinetics but it is difficult to analyse simply anneals carried out at ~ 77°K.

The second annealing stage in alpha plutonium is centred at ~ 160°K and gradual annealing occurs up to room temperature where all but a few percent of the original resistivity increase have annealed. It is found that annealing in delta stabilised plutonium sets in at a lower temperature than in alpha plutonium, that the first annealing stage in delta plutonium is enhanced at the expense of the second stage and that a largerpercentage of the resistivity increase remained unannealed after warming to room temperature.

None of the theories proposed to explain the low temperature properties of plutonium has as yet gained universal acceptance and it is therefore difficult to give an unequivocal explanation of the results presented in this thesis. The various theories of the low temperature properties of plutonium are reviewed and discussed and it is shown that the behaviour of alpha and delta stabilised plutonium during self-irradiation may be best explained by assuming that they are both anti-ferromagnetic at low temperatures. Such an assumption is not unreasonable in view of the close similarity between the actinide and lanthanide series of metals.

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INTRODUCTION

Plutonium, the artificially made element number ninety-four, was first produced in 1943 as part of the wartime Manhattan Project. Using milligram quantities of metal the early workers found that plutonium apparently possessed a variable density, equally reliable evidence being found for values of ~16 and ~19.5 gm/cc. Although this anomaly was later explained when it was found that plutonium had at least five phases between room temperature and its melting point, it provided a foretaste of the many irregularities later found in the physical properties of this remarkable metal.

Today, two decades later, plutonium exists in mega-gram quantities and its uses for both military and peaceful purposes are well known and widely discussed. The causes of many of its anomalous physical properties are, however, still unknown and the problems they present claim the attention of many physicists and metallurgists. The study of these properties is restricted to about a dozen laboratories, excluding an unknown number in the U.S.S.R. This is because of two basic nuclear properties possessed by plutonium; it is fissionable and it is an alpha emitter. The first of these properties is not a very serious barrier, as amounts handled can easily be restricted to a total mass which is smaller than the critical mass by a suitably large safety factor.

The alpha activity of plutonium presents a much more serious obstacle to its safe handling. The range of an alpha particle emitted by the decay of a Pu. 239 nucleus is only a few centimeters in air or

about 50 microns in body tissue. Thus an alpha particle emitted from a nucleus outside the human body presents little or no danger. If however a particle of plutonium becomes chemically deposited inside the body the alpha particles it produces can cause severe biological damage to the surrounding tissue. The toxicity of plutonium is such that the maximum total body burden permitted is 0.6 microgram and to prevent the occurrence of such concentrations in those working regularly with plutonium the maximum limit of airborne contamination is set at 10^{-11} micrograms/cc.

Such levels can be very quickly exceeded if plutonium is exposed to the atmosphere in the open laboratory as it oxidises rapidly, especially in the presence of moisture. This oxide is non-adherent and forms a very fine powder which can rapidly disperse and contaminate the surrounding atmosphere. Accordingly a policy of complete containment has been adopted by most laboratories working with plutonium. All operations are carried out inside air tight glove boxes which are maintained at a slightly negative pressure with respect to atmospheric so that any leaks shall be into the glove box and not out into the laboratory. As plutonium is pyrophoric when in a finely divided form, the glove boxes have an atmosphere of argon or nitrogen. Access to the inside of these glove boxes is effected by the use of long sleeved rubber gloves, sealed to ports in the transparent faces of the box. Transfer of specimens from one glove box to another is accomplished by the use of thermosealed p.v.c. bag techniques.

Such handling facilities exist in the Plutonium Metallurgy Division of the A.E.R.E., Harwell, and for many years now these

facilities have been made available to certain members of the Clarendon Laboratory, Oxford, in order that research on the low temperature properties of plutonium and other actinide metals can be carried out jointly by members of these two laboratories. The first results of this collaboration were presented by Meaden (thesis 1961). In the present thesis we describe further results obtained by us under this arrangement.

Our results deal mainly with the effect of self-irradiation on the low temperature electrical resistivity of alpha and delta stabilised plutonium. A few preliminary experiments have also been performed on uranium 233 and neptunium 237.

In Chapter 1 we give a brief survey of the theory of the electrical resistance in metals and show some of the limitations found when the theory is applied to multivalent metals. We also include an introduction to the basic ideas of radiation damage theory and then conclude the chapter with a review of the low temperature properties of the actinide series of metals, especially plutonium. We have discussed the properties of plutonium at length at this stage of our thesis in the hope that the results which follow may be more easily understood. In Chapter 2 we describe the apparatus and experimental techniques used in our self-irradiation damage experiments and in Chapter 3 we indicate the way in which the resistivity of alpha plutonium increases during low temperature self-irradiation. In Chapter 4 we show that the resistivity of delta stabilised plutonium also increases when held at low temperatures, but in a different manner to that found for alpha plutonium. In Chapters 5 and 6 the results of isochronal

and isothermal annealing experiments are described and analysed to show that second order kinetics are obeyed at $\sim 90^{\circ}K$. In Chapter 7 we present results on plutonium which do not fit easily into any of the earlier chapters, together with some preliminary results on the self-irradiation of uranium 233 and neptunium 237. In Chapter 8 we summarise the results obtained by other workers on low temperature self-irradiation effects in plutonium and make such comments and comparisons as are immediately relevant. Further discussions of our results are held in Chapter 9 and where possible they are interpreted in terms of existing theories of the low temperature behaviour of plutonium.

In Appendices I and II we give details of the specimens used in our experiments and of the actual measurements taken in certain experiments, while in Appendix III we outline the method of Meechan and Brinkman which we used to calculate the activation energy of the $\sim 90^{\circ}K$ annealing stage. Finally in Appendix IV we give a detailed calculation of the number of atoms involved in possible spike effects in alpha and delta stabilised plutonium.

CHAPTER 1

A Review of the Theories of the Electrical Resistance and Radiation Damage Properties of Metals with regard to their applicability to the Actinide Series of Elements

We shall not attempt to provide here a rigorous and comprehensive account of the development of modern theories of the electrical resistance of metals, but rather to examine the applicability of some of the results obtained from these theories. We shall also introduce very briefly some of the basic concepts used in describing the effect of fast particle irradiation on the physical properties of metals.

Finally we shall present a review of the low temperature properties of the actinide series of metals, especially those of the artificially made element number 94, plutonium. Current theories of the low temperature properties of plutonium will be presented in order that the reader may be familiarised with this rather specialised branch of low temperature physics.

1.1. Basic Theories of the Electrical Resistance in Metals

The first attempts made to construct a theory of the transport properties of metals were those by Drude (1900) and Lorentz (1905) who pictured the valency electrons as being detached from their atoms and able to move quite freely as in a perfect gas. They assumed that collisions between electrons could be neglected in comparison with collisions between the electrons and the thermal vibrations and imperfections of the lattice.

By defining the relaxation time, τ, as the time constant of the exponential decay of the distribution function on removal of an external field, it was possible to solve the Maxwell-Boltzman transport equation and obtain for the electrical conductivity σ, the expression:

$$\sigma = \frac{Ne^2\tau}{m} \qquad \text{---------- 1}$$

or $$\sigma = Ne\mu \qquad \text{---------- 2}$$

where $$\mu = \frac{e\tau}{m} \qquad \text{---------- 3}$$

where N is the number of electrons per unit volume, m is the mass of an electron, e the charge on an electron and μ the mobility of an electron. Although the free electron theory successfully explained the Weidemann-Franz law, even giving the correct order of magnitude to the constant of proportionality, it predicted a large electronic contribution to the specific heat and gave an incorrect temperature dependence to the resistance at room temperature.

Subsequent application of Fermi-Dirac statistics by Sommerfeld (1928) removed the need for a large electronic specific heat by showing that only a relatively small number of electrons near the Fermi surface were available for conduction processes. Further progress was made by Bloch (1928) who considered the interactions between the conduction electrons and an electric field having the same periodicity as the lattice. It was found that in a perfect lattice at the absolute zero, the mean free path of the electrons was infinite and hence the electrical resistance zero. Finite resistance was caused by anything which destroyed the perfect periodicity of the lattice. The two most common causes of such scattering were found to be:

i) The thermal vibrations of the lattice atoms, the amplitude and scattering efficiency of which are functions of the lattice temperature.

ii) Imperfections in the crystal lattice, such as impurity atoms in solid solution, vacant lattice sites, dislocations and grain boundaries, the scattering efficiency of which is considered temperature independent.

These two main scattering mechanisms are usually considered separately and their contributions summed to give the total resistivity. This statement is known as Matthiessens rule, viz:

$$\rho = \rho_i (T) + \rho_o \qquad \text{——————} 4$$

where ρ_i, the ideal resistivity is a function of the temperature and ρ_o the residual resistivity is independent of T.

A relaxation time τ always exists for impurity scattering because the mass of the irregularity is much greater than that of the conduction electrons. It is however not always possible to specify a relaxation time τ for the thermal scattering processes; indeed it is only possible to calculate τ and its variation with temperature under certain simplifying assumptions. One of the most important of these assumptions is that the Fermi surface is spherical, a condition only nearly satisfied for the monovalent metals. In order to determine the ideal resistance, the probability that an electron is scattered from a state represented by a wave vector $\underline{k}$ to a state represented by the vector $\underline{k}'$ is calculated. Then from the total transition probability for the whole metal, the relaxation time τ is obtained. The various treatments differ in the assumptions made concerning the manner in which the electrons are coupled to the lattice. In the Debye model it was found that the scattering

matrix included a term $\left|\frac{\underline{k} - \underline{k}'}{q}\right|$, q being the magnitude of a wave vector q in reciprocal space. Transitions for which $\underline{k} - \underline{k}' + q = 0$ are known as normal processes and those for which $\underline{k} - \underline{k}' + q \neq 0$ are known as Umklapp processes. The inclusion of Umklap processes further complicates the calculations but improves agreement between theoretical and experimental results. (Ziman 1954)

Although no relaxation time can strictly be defined at low temperatures, an approximate solution for the ideal resistivity was given by Bloch (1929) who showed that at the lowest temperatures $\rho_i \propto T^5$. Gruneisen (1933) suggested that the equation derived by Bloch for low temperatures might, as it becomes linear in T at high temperatures, also be valid in the intermediate temperature range. This Gruneisen-Bloch relationship,

$$\rho_i = \alpha \Theta_R \left(\frac{T}{\Theta_R}\right)^5 \int_0^{\Theta_R/T} \frac{z^5\, dz}{(e^z - 1)(1 - e^{-z})} \qquad 5$$

where $z = \frac{\Theta_R}{T}$,

is found to hold quite well for a number of metals, among them Gold $\Theta_R = 175^\circ K$, Sodium $\Theta_R = 202^\circ K$, Copper $\Theta_R = 333^\circ K$, Aluminium $\Theta_R = 395^\circ K$ and Nickel $\Theta_R = 472^\circ K$. It is found that Θ_R varies with temperature for most metals and it is usual to plot $\Theta_R/\Theta_{Lim.}$ as a function of $T/\Theta_{Lim.}$ to show the departure from Gruneisen-Bloch behaviour. ($\Theta_{Lim.}$ is the value of Θ_R at $T = \Theta_R$). Only for sodium is it possible to specify a unique Θ_R at all temperatures. The low temperature relationship $\rho_i \propto T^5$ is found to hold for the monovalent metals and also for some divalent metals. However in the transition metals the index sometimes falls as low as 2 and Meaden has shown that for the actinide metals it varies between 2 and 3. It is also found that at high temperatures ρ_i/T

increases with increasing T and for simple metals such as copper this is thought to be a result of the decrease in Θ_D caused by the thermal expansion of the lattice.

The theories described so far have been found to give reasonable agreement with the experimental results for the monovalent and some divalent metals. For most di- and multivalent metals, however, the Fermi surface is found to overlap two or more Brillouin zones with a consequent departure from the spherical shape assumed so far. The use of two zone theory with its concepts of effective mass and hole conduction has produced reasonable agreement with experimental results for bismuth and certain other metals. The resistivities of the transition metals have also been qualitatively explained on two band theory. These metals are characterised by an unfilled inner d shell and Mott (1936) has explained their high resistivities by assuming that a broad low density of states band overlaps the narrow high density of states d band and that the conduction electrons, which are mainly s electrons with an effective mass similar to that of a free electron, have a high probability of being scattered into the narrow d band. Once scattered into a vacant state in the d band, an electron contributes little to the conduction process because of its large effective mass. Thus the number of current carrying s electrons is reduced and there is a consequent rise in the electrical resistivity.

It is found that at high temperatures the resistance of some of the transition metals, especially Pt and Pd increases less rapidly than is required by the relationship $\rho_i \propto T$. Mott explains this by assuming that the d band is nearly full and that there is a rapid decrease in N(E)

as E increases. The probability of an electron being scattered from an s state to a d state is proportional to N(E) in the d band in a range of energies kT at the Fermi surface. Then at high temperatures the electrons with high energies have a smaller probability of being scattered than those of low energy, and the efficiency of the interband scattering process decreases.

A further consequence of the unfilled d shell of the transition metals is the occurrance of ferro- and antiferromagnetism in some of these metals. Mott (1936) and Mott and Stevens (1957) describe the ferromagnetic behaviour of Ni, Co, and Pd, in terms of a collective band model of the electrons which produce the spontaneous magnetisation. At low temperatures only half the conduction electrons, those with spins antiparallel to the spontaneous magnetisation, can be scattered into the d band, whereas above the Curie temperature electrons of both spin orientation can be scattered into the d band, so giving a larger interband scattering resistance.

This model is however not applicable to the other "magnetic" transition metals or to the metals of the rare earth group. The magnetic properties of many of these metals can be explained by assuming that there exists an exchange interaction between the conduction electrons and unpaired "magnetic" electrons localised on certain atoms. Above a critical temperature these localised spins are randomly orientated and the disordered exchange field in a lattice containing such atoms scatters the conduction electrons producing a large magnetic resistivity which, to a first approximation, is independent of temperature. On cooling through this critical temperature, Curie for ferromagnetic, Neel for

antiferromagnetic ordering, the spins start to allign themselves and there is a drop in the magnetic resistivity. The magnetic resistivity is proportional to the degree of order of the spin system and is zero when and if the spins become completely ordered at the absolute zero. The presence of physical or chemical impurities in the specimen will inhibit perfect ordering at absolute zero and lead to a large residual "magnetic" resistivity many times larger than the normal residual resistivity.

Such behaviour is widespread in the rare earth group of elements with their unfilled 4f shells and it is found that spin disorder scattering is most important for those metals with a low Debye temperature. Dysprosium for example shows ferro- antiferro- and paramagnetic behaviour over different temperature ranges. The hexagonal close packed structure of the majority of the rare earth metals does not lend itself to the description of antiferromagnetic ordering in terms of two interpenetrating cubic sub-lattices of opposite spin which is used to describe the structure of Mn. O. The ordered state of these metals can, however, be described in terms of a helical or sinusoidal variation of spin orientation about the c axis of the crystal. Reviews on the subject of magnetic ordering in the transition and rare-earth series of metals have been given by Coles (1958), Jones (1956), Mott and Stevens (1957) and Elliott (1961).

It is found that not all of the metals in the transition and rare earth series of metals can be described in terms of either of these models and an intermediate model has been advanced by Blandin and Friedel (1959) to account for transition impurities in the noble metals. It supposes that

electrons can exist in virtual bound states when the ionic potential is not sufficiently attractive for the 4f electrons to occupy bound states. A similar model has been used by Hocker (1962) to explain the resistivity of cerium, of ytterbium under pressure and possibly plutonium.

Finally in this review of the electrical resistance in metals we should like to reconsider the statement of Matthiessen's rule,

$$\rho = \rho_0 + \rho_i (T)$$

This relationship holds for small impurity concentrations if:
i) the thermal vibrations of the foreign atoms give the same scattering as those of the solvent metal, and:
ii) the effective number of current carriers is unaltered by the addition of foreign atoms.

These conditions are usually only approximately satisfied and Koehler (1949) has shown that deviations from Matthiessen's rule should theoretically be positive, i.e. the resistance due to impurity scattering should increase with increase in temperature. That this is true for most metals is shown by the work of Krautz and Schultz (1954 and 1957) and Alley and Serin (1959). Other deviations from Matthiessen's rule are known to exist, Chandrasekhar and Hulm (1958) for example, show that the impurity resistance of α and γ uranium alloys decreases markedly with increase in temperature. They explain this by assuming that the resistivity is due to scattering of the conduction electrons into a narrow d band whose density of states at the Fermi level, Nd (ζ) decreases with increasing temperature. They furthermore show that for high enough solute concentrations the decrease in impurity resistance

can become greater than the increase in ideal resistance leading to a net decrease in resistance with increase in temperature.

One further type of deviation from Matthiessen's rule can be found in those metals which show ferro- or antiferromagnetic ordering. The magnetic resistance is usually considered constant above the transition temperature and Matthiessen's rule can be written $\rho = \rho_i + \rho_o + \rho_{mag.}$ However below the transition temperature, $\rho_{mag.}$ is strongly temperature dependent. Furthermore the presence of a small concentration of certain impurities can inhibit perfect alignment of the spins at low temperatures and give rise to a large residual resistance which cannot be identified with the true temperature independent impurity resistance. Thus great care must be taken when attempting to split up the resistances of such metals into separate components.

Comprehensive reviews of the theory of the electrical resistance in metals have been given by Mott and Jones (1936), Wilson (1953) and Jones (1956).

1.2. A short Introduction to Irradiation Effects in Metals

It is impossible to give here more than a very brief introduction to what is a vast and complex field of research in which pure research and reactor technology have become inextricably mixed. Many reviews of this subject exist, including those of Seitz and Koehler (1956), Dienes and Vineyard (1957) and Billington and Crawford (1961).

When an energetic particle traverses the lattice of a crystalline solid it can lose its energy by several processes, the most important of which is by elastic collision with the lattice atoms. If the energy

received by the lattice atom, E_p, is greater than its displacement or Wigner energy, E_d, it is displaced from its lattice site. Unless the displaced atom immediately combines with a nearby vacancy, it comes to rest in an interstitial position to produce, with the vacancy formed by its creation, a Frenkel pair. As the recoil takes place before the neighbouring atoms have time to relax, the value of E_d, 10-30 eV for a typical monatonic solid, is considerably larger than the energy required to form a Frenkel pair by a thermo-dynamically reversible process, 3 to 6 eV. In many cases the energy transferred to the recoil atom by this primary collision is much greater than E_d and the primary recoil atom is capable of causing further displacements. This process is repeated until the energy of the recoiling atom becomes less than E_d and no more displacements can be made. This displacement cascade accounts for most of the damage produced during heavy particle (not electron) bombardment. The number of displacements resulting from a single primary particle of energy E_p is denoted by $\nu(E_p)$ and for $E_p \gg E_d$ Kinchin and Pease (1955) have given the relation $\nu(E_p) = E_p/2E_d$. For common metals however this has been found to be too high by a factor of two or more.

A further possible mechanism arises during neutron bombardment when impurity atoms can be formed by transmutation. Similarly, the radioactive decay of a metal such as plutonium leads to the build up of its daughter products which can, over long periods of time, reduce the purity of the sample.

Ionisation of lattice atoms is also possible if the bombarding particle has a high enough energy and such effects can be important in insulators, dielectrics and ionic crystals, but are not considered

important in good conductors. A further mechanism which is important in polyatomic solids and super lattice alloys is that of replacement collisions in which the bombarding particle ejects an atom from a lattice site, but having insufficient kinetic energy to escape falls into the vacancy it has created.

An alternative model of irradiation damage in solids proposed by Seitz (Seitz & Koehler, 1956) and Brinkman (1954) considers the consequences of the release in a small volume of the large amount of energy possessed by a bombarding particle. A region of material around the track of the particle is thought to rise rapidly in temperature to $\sim 1{,}000^{\circ}K$ for about 10^{-10} seconds when enough energy is transferred to the lattice atoms to make them vibrate violently without being displaced. This region, known as a thermal spike, expands and cools rapidly but is considered to be in existence long enough for atomic interchange, rearrangement into new high temperature phases or thermal generation of Frenkel defects to occur. At the end of such a thermal spike the energy of the particle falls below a certain critical value and the mean free path between displacement collisions becomes of the same order as the atomic spacing. Each collision then results in a displaced atom and towards the end of its track the particle produces a volume of about 10^3 atoms which undergoes severe local melting and turbulence. Definite evidence for the existence of thermal and displacement spikes is difficult to obtain, but firm evidence exists for the concept of a further type of spike, the fission fragment spike. Whereas thermal and displacement spikes involve relatively few atoms and are approximately spherical, the spikes produced by fission fragments

are by comparison large cylinders around the axis of the fission fragment. track and involve large numbers of displaced atoms.

In the mechanisms discussed so far, no account has been taken of the ordered arrangement of atoms on a crystal lattice. Silsbee (1957) has demonstrated that focusing collisions in a close packed lattice can lead to the absorption of energy transfers greater than E_d without producing additional displaced atoms. Such a mechanism could reduce the number of displacements predicted by cascade theory to a more reasonable number. A further mechanism which depends on the lattice structure is that of the "dynamic crowdion", whose existence was postulated by Thompson (1956) to explain the transport of certain interstitials large distances from the point of impact of a primary neutron collision.

Although direct observation of the nature of radiation damage is sometimes possible at room temperature and above, using the electron microscope and other sophisticated techniques, the majority of radiation damage experiments, especially at low temperatures, involve the measurement of some common physical property. The nature of the damage processes involved is then deduced from the observed changes in this property. Perhaps the most commonly observed property is the electrical resistivity, especially the residual resistivity, changes in which during and after annealing shed some light on the temperatures and activation energies of the recovery processes involved. It is however often impossible to determine the precise nature of these recovery processes solely from such observations. Further measurements of the thermal conductivity, heat capacity, expansion coefficient, Hall coefficient, etc., can sometimes help to elucidate the problem by reducing the number of

TABLE 1.1.

A summary of some of the properties of the actinide group of elements

	Electronic Structure Rn. shell+	M.P. °C	Density g/cc.	Crystal Structure	Expansion Coeff't. $m\mu/^{\circ}C.10^{6}$	Resistivity ρ $\mu\Omega.cm.10^{6}$	$\frac{1}{\rho}\frac{d\rho}{dt}.10^{5}$	T_c °K	⊗R at 20°K °K	⊗R at 300°K °K
^{89}Ac.	$5f^{0}6d^{1}7s^{2}$	~1050	~ 10	f.c.c.	-	-	-	-	-	-
^{90}Th. α	$5f^{0}6d^{2}7s^{2}$	-	11.72	f.c.c.	+12	13	+396	1.37	108	135
β	"	~1690	11.00	b.c.c.	-	-	-	-	-	-
^{91}Pa.	$5f^{2}6d^{1}7s^{2}$	<1873	15.37	tetragonal	-	-	-	-	-	-
^{92}U. α	$5f^{3}6d^{1}7s^{2}$	-	19.	orthorhomb.	+19	~ 30	+500 to +50	0.3 to 1.3	101	60
β	"	-	18.1	tetragonal	+22	54	+18	-	-	-
γ	"	1130	17.9	b.c.c.	+18	50	+73	-	-	-
^{93}Np. α	$5f^{4}6d^{1}7s^{2}$	-	20.45	orthorhomb.	+27.5	114	+6 to +0	<0.44	137	-
β	"	-	19.36	tetragonal	+41	107	+31 to +0	-	-	-
γ	"	639	17.90	b.c.c.	+33	109	-6	-	-	-
^{94}Pu. α	$5f^{5}6d^{1}7s^{2}$	-	19.82	monoclinic.	+55	145	-21	<0.50	-	-
β	"	-	17.80	b.c.monocl.	+40	110.5	-6	-	-	-
γ	"	-	17.14	orthorhomb.	+35	110	-5	-	-	-
δ	"	-	15.92	f.c.c.	-9	103	+7	-	-	-
δ'	"	-	16.00	f.c.tetrag.	-16	105	+45	-	-	-
ε	"	639.5	16.51	b.c.c.	+36	114	+7	-	-	-
^{95}Am.	$5f^{6}6d^{1}7s^{2}$	830 ?	11.87	double h.c.p.	-	-	-	-	-	-

unknown parameters. Our choice of electrical resistance as the property with which to study the self-irradiation of plutonium was influenced by two factors. Firstly, the necessity of using long self-irradiation periods at low temperatures restricted measurements to those which could be performed on canned samples, and secondly, previous work on the low temperature resistance of plutonium had left a number of unsolved problems which required further investigation.

1.3. An Introduction to the Low Temperature Properties of the Actinide Metals

The actinide series of metals strongly resembles the lanthanide or rare earth series in having incomplete inner electron shells which are progressively filled on passing along the series. In the lanthanide series it is the 4f shell which is filled while the 5d shell remains partly filled; in the actinide series the corresponding shells are the 5f and 6d respectively. The physical properties of the actinide metals become progressively more anomalous as the atomic number increases. In Table 1.1. we give a review of some of the more important of these properties, the data being taken from Waldron (1964) and Meaden (Thesis, 1964). Little is known of the properties of the elements actinium (89), protoactinium (91) and americium (95) because only extremely small quantities have been prepared in metallic form. Thorium (90) and uranium (92) are available in large quantities and in high purity forms produced by the van Arkel - de Boer and Blumenthal techniques respectively. The common isotopes of these metals may be safely handled in the open laboratory, neptunium (93) and plutonium (94), however, have to be handled under

special conditions because of their dangerous α activity. Plutonium, because of its civil and military importance is now available in large quantities and small amounts of high purity experimental material are becoming available for research purposes. It should be noted however that material initially of high purity can rapidly build up considerable impurity concentrations of its daughter products as a result of the radioactive decay of some of its atoms. Americium 241, for example, is produced at an initial rate of about 10 p.p.m. per month as a result of the β decay of $Pu.^{241}$. Finally neptunium is available in small quantities of relatively low purity metal which was extracted from the residues of the plutonium extraction plant at Windscale.

1.3.a. Thorium

The physical properties of thorium may be considered as a reference from which to discuss the abnormalities of the succeeding actinide metals. Its electrical resistivity has been shown by Meaden (Thesis 1961) to follow the Grunaisen-Bloch relation with Θ_R = 135° K over a wide range of temperatures. Only at very low temperatures does Θ_R fall to ~ 106° K. Below ~ 26°K the ideal resistivity is given by $\rho_i \propto T^n$ where $n \approx 3.0$ Thorium is also a superconductor with a transition temperature of ~ 1.35°K. Its low electrical resistivity and the lack of an unusually large electronic specific heat signify a low density of states at the Fermi level, $N(E)_\zeta$, and its small thermo-electric power suggests that $\frac{d\,N(E)}{d\,E}\Big|_\zeta$ is also small.

1.3.b. Uranium

Uranium too is found to be a superconductor but its transition

temperature decreases from ~ 1.3°K for a pure specimen to 0.3°K or lower for an impure specimen; the transition width also being larger for the impure specimen. At low temperatures $\rho_i \propto T^n$ with the index n = 3.1 similar to that observed for thorium. The resistivity is found to increase less rapidly than given by $\rho_i \propto T$ and consequently Θ_R falls monotonically from 101°K at 20°K to ~ 60°K at room temperature. The high resistivity and high electronic specific heat, $\gamma = 2.6 \times 10^{-3}$ cal./mole./deg.^{2}, point to a high density of states at the Fermi surface. Chandrasekhar and Hulm (1956) and Meaden (Thesis 1961) have explained the decrease of Θ_R with increase in T by assuming, after Jones (1956), that the Fermi level E_ζ is dependent on temperature. The large positive thermoelectric power suggests also that $\frac{d N(E)}{d E}\Big|_\zeta$ is positive

1.3.c. Neptunium

Neptunium does not become superconducting at temperatures down to 0.41°K and like thorium and uranium it obeys the law $\rho_i \propto T^n$ below ~ 30°K with n = 3.1. The temperature coefficient of resistance of neptunium is found to decrease steadily as the temperature increases, becoming virtually zero at the α-β phase change. Thus the departure from Gruneisen-Bloch behaviour is even more pronounced than for uranium. The thermoelectric power is found to increase to a maximum of ~ +8 μV/°K on warming to ~ 120°K and then to fall to zero at ~ 260°K and become negative at higher temperatures. Once again its high resistivity and electronic specific heat suggest a high density of states at the Fermi surface. No comprehensive explanation of the properties of neptunium has yet been put forward. The mechanism proposed for uranium may also be operative for neptunium, possibly accentuated by a temperature

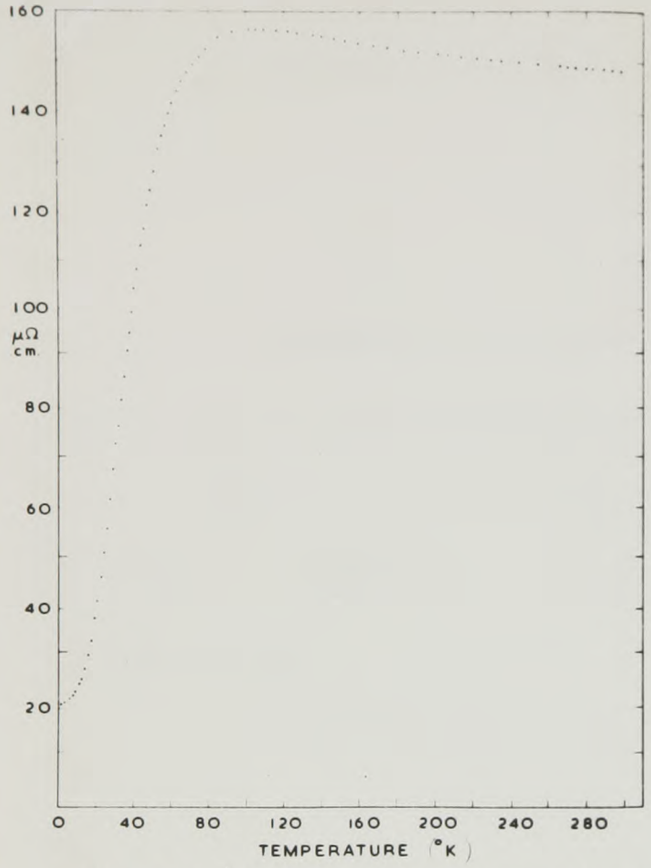


FIG [redacted] ELECTRICAL RESISTIVITY OF Pu 3 (RUN 5)

FIG.1.1

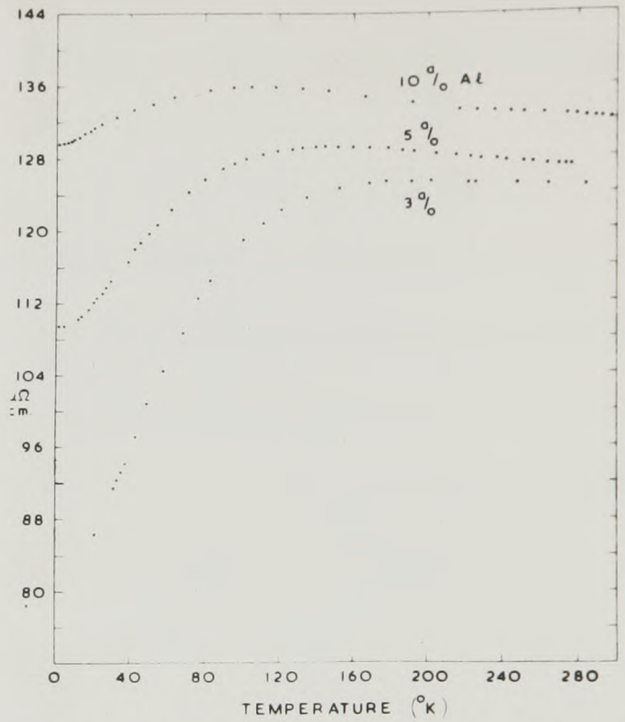


FIG [redacted] ELECTRICAL RESISTIVITY OF δ - Pu-Aℓ ALLOYS

FIG.1.3

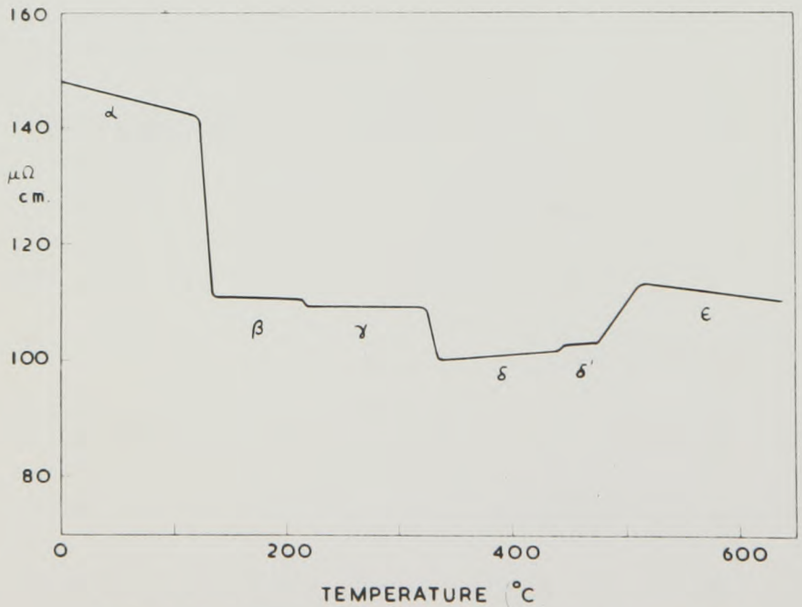


FIG. [redacted]. ELECTRICAL RESISTIVITY OF Pu ABOVE ROOM TEMPERATURE (KING, UNPUBL.)

FIG.1.2

dependent band structure. A review of the physical properties of neptunium has been given by Lee (1961).

1.3.d. Plutonium

Plutonium is unique among metals in having six different crystallographic modifications between room temperature and its low melting point. The stable phase at room temperature and below is the monoclinic alpha phase. The resistivity of α plutonium has been measured down to ~1.7°K by Sandenaw (1958) and Meaden (Lee, Meaden, Hall and King 1960) and is shown in Fig. 1.1. As the temperature rises from zero the resistivity increases rapidly to a maximum at ~ 105°K and then falls steadily until the $\alpha - \beta$ phase change at 395°K. The residual resistivity is found to vary from ~18 $\mu\Omega$cm. for the purest specimens to ~50 $\mu\Omega$cm. for specimens of lower, but still reasonably high, purity. The ideal resistivity is found to obey the relation $\rho_i \propto T^n$ below ~ 30°K with n ranging between 2 and ~ 2.8, the highest indices being found for the purest specimens. The resistivity of the higher temperature phases is shown in Fig. 1.2. in which it can be seen that only the δ and δ' phases have positive temperature coefficients of resistance.

The face centred cubic delta phase can be stabilised to room temperature and below by the addition of certain elements, the most common of which is aluminium. The resistivities of specimens stabilised with various percentages of aluminium are shown in Fig. 1.3. for temperatures below 300°K. As the aluminium content increases the resistivity at any temperature rises and the resistivity maximum moves to lower temperatures. By extrapolating the results of such experiments to zero aluminium content it is possible to construct the hypothetical

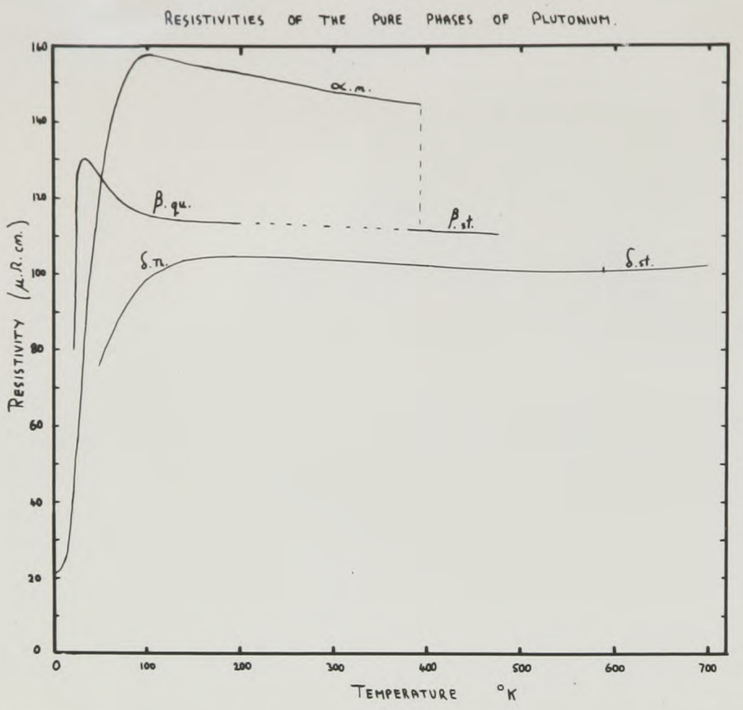


FIG .1.4

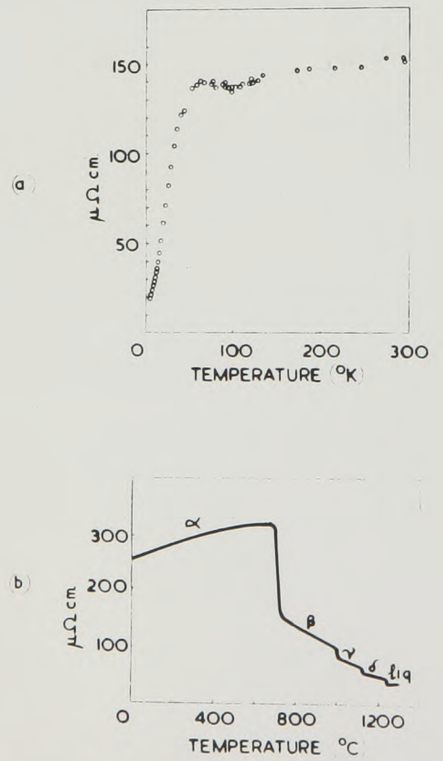


FIG [redacted] ELECTRICAL RESISTIVITY OF MANGANESE
a AFTER WHITE AND WOODS 1957
b) AFTER GRUBE AND SPEIDAL 1940

FIG .1.5

curve for pure delta plutonium. Such a curve is shown in Fig. 1.4., the extrapolation having been performed by Lee (Lee & King 1963). Also shown is a typical curve for α plutonium and a curve obtained for β plutonium by Lee and King (1963). By quenching rapidly from $\sim 420^{\circ}K$ to $\sim 100^{\circ}K$ they found that it was possible to retain the β phase and by further cooling to obtain the curve shown. The three curves show the same characteristics. On lowering the temperature the resistivity first rises slowly to a maximum and then falls sharply. In spite of the widely differing crystal structures it would appear that the same mechanism is operative in all three phases.

One explanation proposed for the low temperature properties of plutonium is that of antiferromagnetic ordering; Sanderow and Olsen (1960), Lee, Maeden and Mendelssohn (1960). The latter authors based their proposal on the similarity between the low temperature resistivities of plutonium and α manganese which is known to be antiferromagnetic. The resistivity of α Mn. is shown in Fig. 1.5. for both low and high temperatures. It can be seen that at low temperatures the curve is very reminiscent of that of α plutonium although the temperature coefficient of resistance of α Mn. is positive for temperatures more than a few degrees above the resistivity maximum. The temperature coefficient of resistance is, however, negative for the high temperature phases of manganese as well as plutonium. Neutron diffraction studies of α manganese by Shull and Wilkinson (1953) showed the Neel point to be at $\sim 100^{\circ}K$, some 20° above the resistivity maximum and also that some short range order persisted to well above room temperature. No anomaly in the magnetic susceptibility of α Mn. can be found near $\sim 100^{\circ}K$

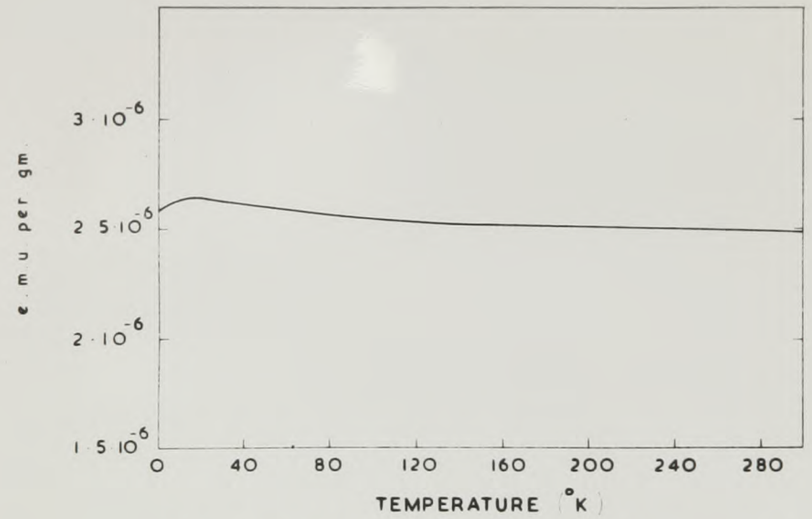
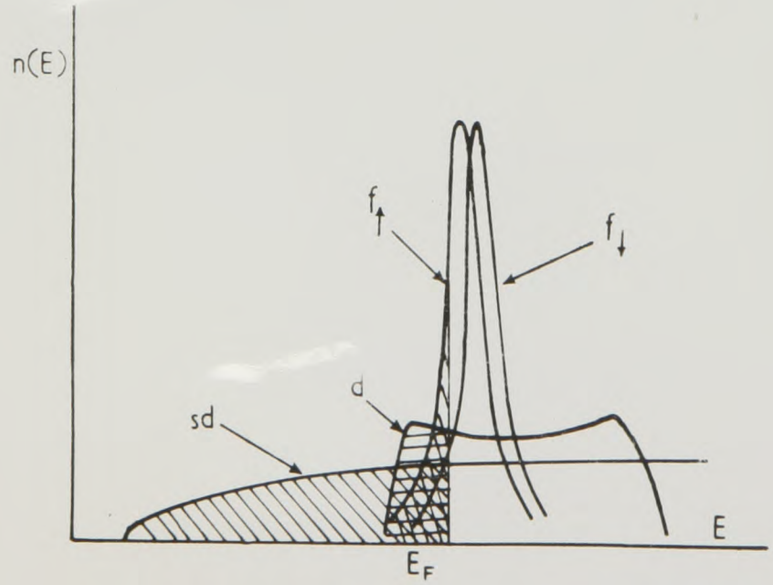


FIG. ■ SUSCEPTIBILITY OF Pu (WEIL et al. 1960)

FIG.1.6



Structure de bande proposée pour le plutonium α.

FIG.1.7

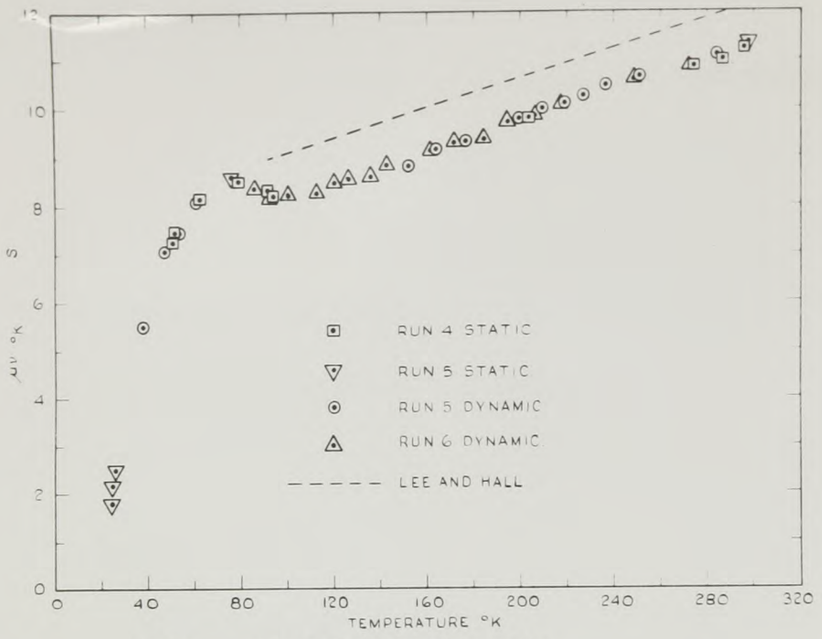


FIG [redacted] THERMOELECTRIC POWER OF Pu

FIG.1.8

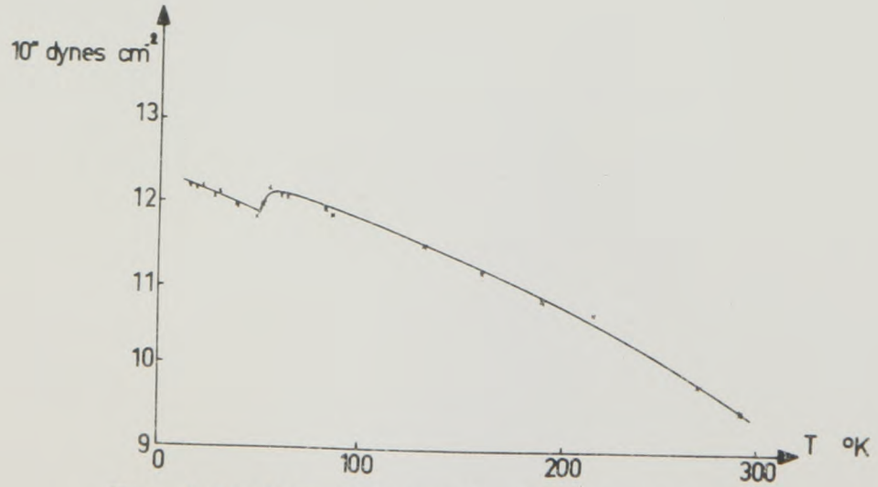


Fig. [redacted]. Module d'Young du plutonium alpha.

FIG.1.9

although there is a small specific heat anomaly at ~ 95°K (Shomate 1945). In the case of α plutonium no anomaly in the magnetic susceptibility is found at temperatures near the resistivity maximum, although as shown in Fig. 1.6. Weil et al. (1960) found a small hump at ~ 20°K. No confirmation of the existence of antiferromagnetism has been obtained from neutron diffraction experiments performed on plutonium at Los Alamos and Harwell. The sensitivity of these experiments was however rather low because of the strong attenuation of the neutron beam by the plutonium sample. Furthermore, no specific heat anomaly has been found at temperatures near the resistivity maximum which cannot be satisfactorily connected with the release of energy stored during low temperature self-irradiation.

Rocher (1962) has also proposed an antiferromagnetic model for the low temperature properties of α plutonium with a Neel temperature at 60°K. By assuming that the 5f level contracts on to the nucleus with a consequent weakening of the interactions between neighbouring atoms, he assumes that virtually bound 5f states can exist in plutonium. Exchange decoupling splits these 5 f states into two sub levels of opposite spin with a difference in population of 0.3 electrons, and a resultant magnetic moment of 0.3 μ B, which is slightly higher than the value of ~ 0.2 μ B found for PuH_2. Rocher supposes that this magnetic moment is sufficient to give magnetic ordering at low temperatures. The band structure obtained from this model is shown in Fig. 1.7. In support of his choice of ~ 65°K as the Neel point, Rocher cites Meaden's thermo-electric power results shown in Fig. 1.8., the change in slope at ~ 65°K indicating the Néel point. Recent results of Lallement (1963) shown in Fig. 1.9.

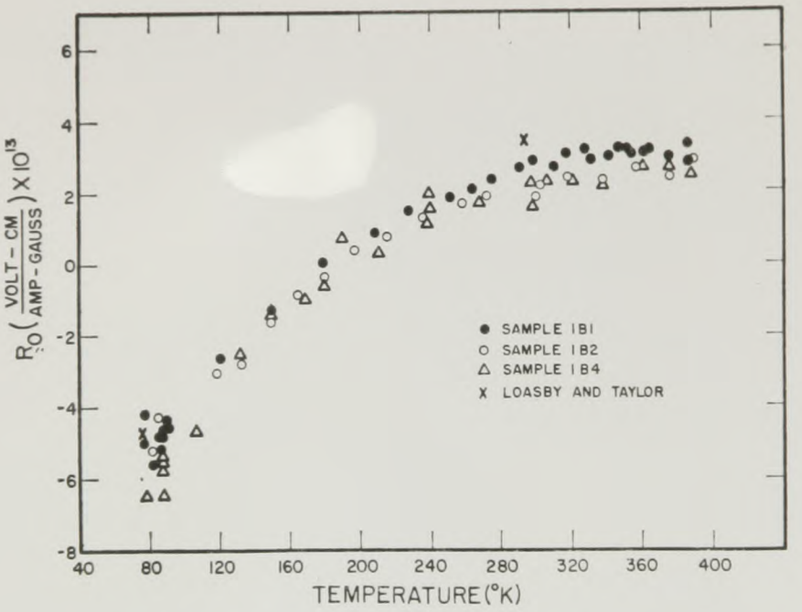


FIG. 1. Hall coefficient of alpha plutonium.

FIG. 1.10

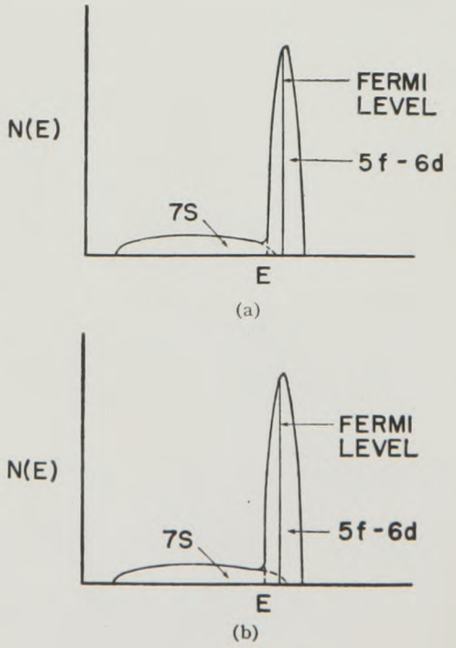


FIG. 2. Proposed band overlap (schematic) with increasing temperature for plutonium; (a)below 190°K, (b) above 190°K.

FIG. 1.11

indicate a minimum in Young's modulus between 50 and 60°K and are interpreted by Lallement in terms of a magnetic order disorder transition.

Other models advanced to explain the physical properties of plutonium reject the idea of antiferromagnetism and interpret the results in terms of interband scattering. By assuming that the band structure consists of a broad low density of states band overlapped by a narrow high density of states band and that the Fermi level is temperature dependent, Lee and Hall (1959) and Smoluchowski (1962) are able to explain the negative temperature coefficient of α plutonium and the alloying behaviour of δ plutonium at high temperatures. In order to explain the resistivity maximum at low temperatures Smoluchowski assumes, following Wilson (1938), that the number of phonons available for interband scattering at low temperatures is drastically reduced by quantum selection rules. No independent information is however available to support this theory.

Hall effect measurements reported by Loasby and Taylor (1961) showed that the Hall coefficient changed from a positive value at room temperature to a negative value at $\sim 77^{\circ}$K. Recent, more detailed results by Brodsky (1963) showed that the Hall coefficient varied continuously with temperature between these extremes, becoming zero at $\sim 200^{\circ}$K (Fig. 1.10.). This change from net electron conduction to net hole conduction at $\sim 200^{\circ}$K is explained by Brodsky on the basis of the band model indicated in Fig. 1.11. At low temperatures the top of the broad 7s band lies below the Fermi level which is slightly below the middle of the narrow 5f - 6d band. As the temperature increases the top of the 7s band broadens due to thermal excitation faster than the

increase in the Fermi level, until the Fermi level is below the top of the 7s band. Electrons can now be excited into the 5f - 6d band leaving holes in the 7s band and leading to a positive Hall coefficient. Furthermore Brodsky observes no field dependence of the Hall coefficient at any of the temperatures measured and deduces that this precludes the existence of a Neel point at $\sim 100^{\circ}K$. As measurements were not made below $\sim 77^{\circ}K$ it does not rule out the possibility of a $60^{\circ}K$ Neel point.

It can be seen from this review that there is no generally agreed cause of the anomalies in the physical properties of plutonium observed at low temperatures. Accordingly we have analysed our results in as many ways as possible and left discussion of their relevance to the general understanding of the properties of plutonium until the final chapter.

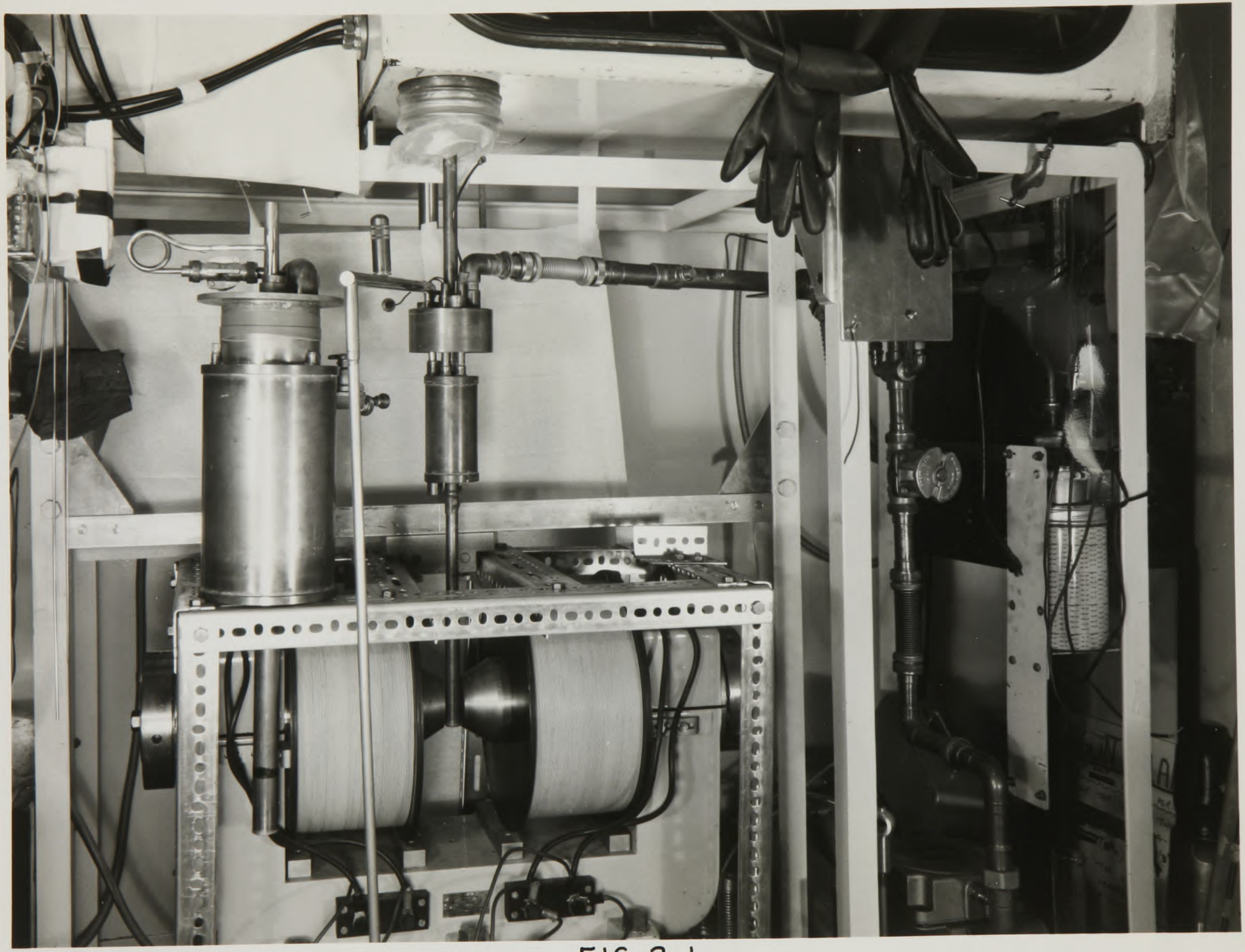


FIG. 2.1.

CHAPTER 2

The Apparatus and Experimental Procedure

As indicated in the introduction, the extreme toxicity of plutonium and neptunium requires that at all times they are contained so as to avoid the spread of radioactive contamination. There are two accepted methods of fulfilling this requirement; the use of glove boxes, or, when circumstances permit, the use of sealed capsules. The relative merits and restrictions of these methods will now be discussed with regard to their suitability for cryogenic experiments.

2.1. The Cryogenic Glove Box

The construction and operation of the standard type of free standing glove box has been fully described both by Lord and Waldron (1957), and in papers read at the Glove Box Symposium (Walton 1958.Ed.). In order to be able to cool active specimens to very low temperatures a cryogenic glove box was designed and built by Meaden and Lee and is described in a paper by them (Meaden and Lee 1960). At the beginning of 1961 this glove box was made available to us and was modified for use in magnetic experiments such as the Hall effect and magneto-resistance. It is shown in its modified form in Fig. 2.1. The essential feature of the design of this glove box is the complete separation of the active specimens, which are suspended inside the long central cryostat tube, and the inactive cryogenic fluids which surround it. The inside of the cryostat tube can be filled with helium exchange gas to give good thermal contact between specimen and coolant or can be evacuated if required by a vacuum system inside the glove box. Furthermore liquid helium can be condensed inside the cryostat tube by surrounding the tube with liquid

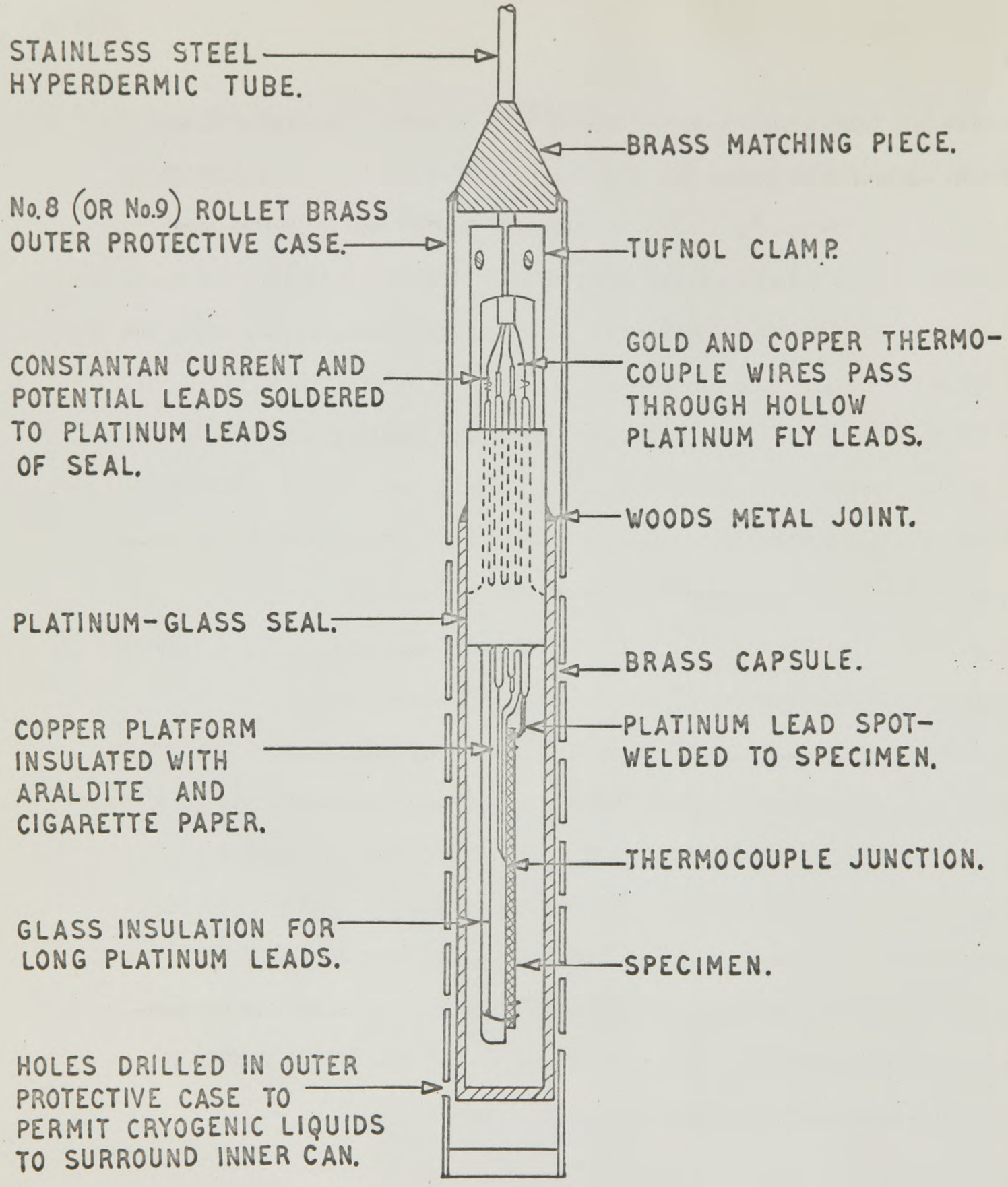


FIG. 2.2 DETAIL OF TYPICAL SPECIMEN SEAL.

helium and then pumping on the liquid and lowering its temperature. Liquid nitrogen or argon can also be liquified around the specimen in a similar manner. Specimens are mounted inside the cryostat tube on a holder suspended at the end of a thin walled German silver tube; access to the specimens being obtained by raising the German silver tube out of the cryostat, and into the glove box proper. When in this position it is possible to mount and demount specimens working through the neoprene gloves attached to the perspex front face of the glove box. One of the main advantages of this system is that repairs can be effected quickly and without removal of the specimen from the glove box. The arrangement was found to be ideal for the measurement of the electrical resistivity and thermoelectric power of specimens from 1.4°K to ~330°K as these measurements could be made dynamically during slow warming or cooling. Its usefulness was reduced to those temperature ranges covered by liquids boiling under normal or reduced pressure if constant temperatures were required. The length of run obtainable with this apparatus was determined by the heat leaks down the cryostat tube and electrical leads and the Joule or self-heat generated by the specimen. Under normal conditions an 8 hour run at 4.2°K was possible from an initial filling of 1½ litres of liquid helium.

Very little use of this glove box was in fact made by us as sealed capsules were found to be much more convenient for self-irradiation damage experiments.

2.2. The Sealed Capsule Method

Sealed capsules were first used for cryogenic purposes by Meaden in the search for superconductivity in neptunium and plutonium (Lee,

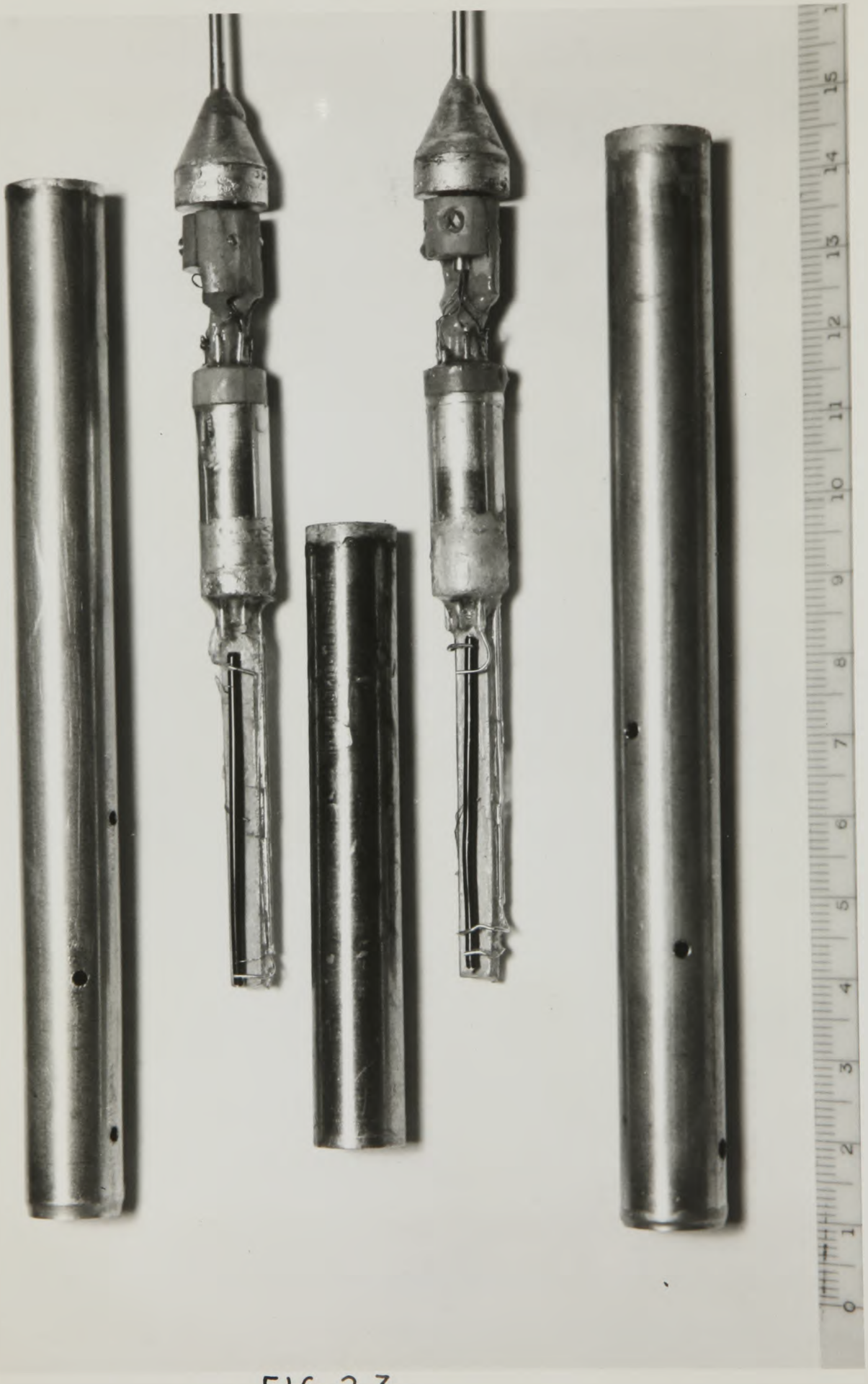


FIG. 2.3.

Meaden and Mendelssohn, 1959) and have been described by Meaden and Lee, (1960). A few capsules of this type were used by us in our initial experiments on self-irradiation damage at low temperatures. As the work proceeded various improvements were made to this basic design to increase its mechanical reliability and to enable the temperature of the specimen to be more closely controlled and more accurately measured. The major improvement was in the use of fly lead seals which enabled the thermocouple junction to be inside the capsule actually on the specimen and not merely attached to the outside of the capsule as with the earlier type of seal. In Fig. 2.2. a typical seal assembly is shown in diagrammatic form while Fig 2.3. shows a photograph of two such assemblies with their inner capsules and outer protective cases. The seal itself was made from a 2.5 cm. length of 1 cm. diameter platinum tubing through the middle of which 4 (or2) lengths of 30 thou. O.D., 10 thou. I.D. platinum tube and 2 (or 4) lengths of 20 thou. diameter platinum wire were sealed with lead glass. In the case of the seal with 4 fly leads, the potential leads as well as the thermocouple wires passed continuously through the seal. We found that it was extremely important to use Woods metal when soldering the wires into the hollow platinum tubes as the gold - 2.1 At.% cobalt thermocouple wire dissolved in soft solder. The purpose of the copper platform was to reduce as far as possible temperature gradients along the length of the specimen. It was found that a layer of cigarette paper attached to the copper platform by a thin layer of surface coating Araldite adequately insulated the specimen from the copper. In order to facilitate encapsulation the relevent parts of the platinum seal and brass capsule were pre-tinned with Woods metal. Other details of the seal are shown in Fig. 2.2.

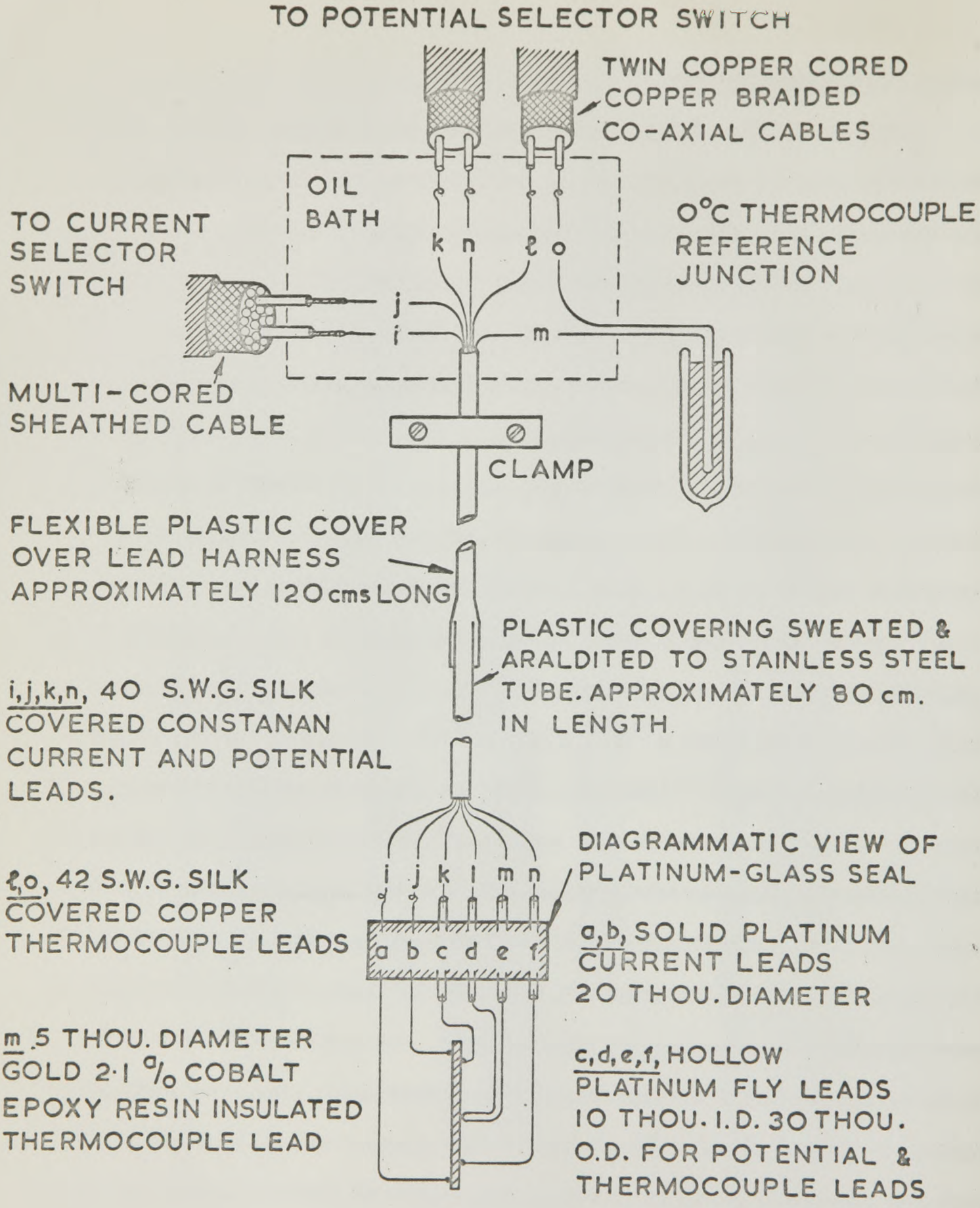


FIG.24 DETAIL OF LEAD SYSTEM

2.3. The Wiring System

Details of the wiring system used are shown in Fig. 2.4. The total length of the lead harness, about 2 meters, was determined by the requirement that it should be possible physically to transfer a specimen from one 16 litre Dupree Swift to another and hence the harness was somewhat longer than twice the depth of a Dupree Swift. The 40 s.w.g. double silk covered constantan current and potential leads were insulated from the thermocouple wires and each other by coatings of either Durofix diluted with acetone or Shellac dissolved in methyl alcohol. However, trouble was experienced due to the breakdown of this insulation and we would suggest that enamelled and silk covered wires formed into a harness with an epoxy resin paint would provide better lead insulation. The lower part of the lead harness was encased in a stainless steel hypodermic tube for physical protection. The earliest rigs used 2 cm. diameter thin walled German silver tubes for this purpose but this led to a premature ending of the first 5000 hour run on α Pu.2. when the German silver tube bent and cut into the leads, causing them to short together. Rather than risk further accidents of this type, later rigs used the thicker and stronger stainless steel hypodermic tubing which gave rise to a slightly larger heat leak. Although the majority of the leads in the potential measuring circuit were made of copper to reduce parasitic thermal e.m.f's to a minimum, 40 s.w.g. constantan wires were used for potential leads in the harness. To have used copper leads would have produced an increase of approximately 25% in the heat leak to the specimen. In table 2.A. we give the approximate heat leaks of the various components, assuming a path of $\sim$70 cm. between $4^{\circ}K$ and $300^{\circ}K$ and

the mean thermal conductivity values given by White (1959), page 186. We include also the boil off rate of liquid helium caused by these heat leaks and by the self heating of two typical plutonium specimens.

TABLE 2.A.

Component	Heat Leak (mW)	Helium evaporation rate (cc./hr.)
1 x 2 mm. O.D. G./s. tube	3.4	4.5
1 x 2 mm. O.D. S./s. tube	5.0	6.6
1 x 40 s.w.g. Cu. wire	1.8	2.4
1 x 5 thou Au.2.1 At.% Co. wire	1.0	1.3
4 x 40 s.w.g. Const. wires	0.8	1.9_5
1.8 gm. Pu. @ 2.2 mW/gm.	4.0	5.3
0.25 gm. Pu. @ 1.95 mW/gm.(Pu.12)	0.5	0.6_5
Total for white rig with Pu.12. S./s. tube	9.1	12.0
Assuming latent heat of vapourisation of helium gas at $4.2^{\circ}K$ = 0.65 cal./cc. giving boil off rate of liquid helium = 1.3_2 cc./mW. hr.		

It will be shown in Fig 2.11. that Helium dewar 2 had a boil off rate of 30.8 cc./hr. (740 cc./day) with 3 plutonium specimens and 25.6 cc./hr. (613 cc./day) with 2 plutonium specimens. This gives a difference of 5.2 cc./hr. for the extra specimen, Pu. 12. compared with our calculated value of 12 cc./hr. However in our calculation no allowance was made for the cooling effect of the cold helium gas passing up the neck of the dewar. It would appear that this cooling effect reduces the heat leak down the harness and stainless steel tube by about a factor of 2.

Other relevant details of the wiring system may be found in Fig.2.4.

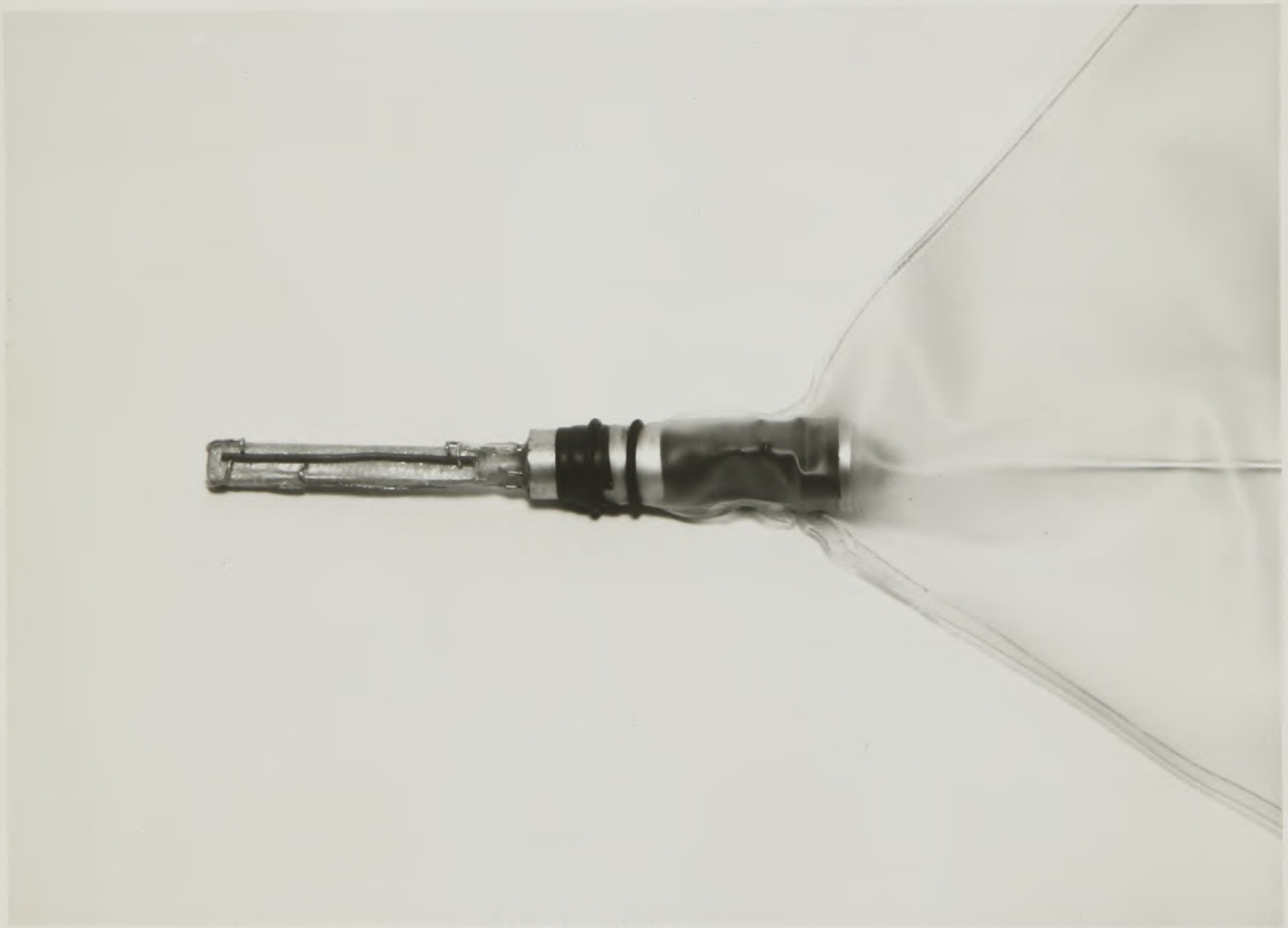


FIG. 2.5.

2.4. The Encapsulation and Decontamination Procedure

Encapsulation and decontamination of specimens mounted on the original solid lead seals was considerably simpler tasks than for specimens mounted on the subsequent fly lead seals. The principles involved are however the same and will be illustrated by reference to the procedure for the original seals.

The outside of the brass capsule and that part of the metal - glass seal not pre-tinned with Woods metal were coated with a thin layer of Shellac which was allowed to dry before these components were posted into the glove box used for encapsulation. After the current and potential leads had been spot welded to the specimen, the seal was carefully Woods metalled into the neck of the brass capsule. It was then posted out of the glove box in a p.v.c. bag and removed to a fume hood for decontamination. In the fume hood the sealed capsule was removed from the p.v.c. bag and the Shellac dissolved away in methyl alcohol removing with it such contamination as had been picked up from inside the glove box.

The use of fly lead seals necessitated a considerable revision of the encapsulation procedure, but a method was evolved which, although somewhat laborious, proved reliable. A standard 8" diameter p.v.c. posting-in bag was shaped down at one end to a small tube just large enough to allow the 1 cm. diameter platinum seal to pass through. This is shown in Fig. 2.5. The p.v.c. tube was cut to cover all but about 1 cm. of the platinum tube and then bound on to the platinum by a strip of "Lasovic" p.v.c. tape and a pair of rubber O rings. This formed a seal which was both activity and gas tight. The pre-tinned part of the

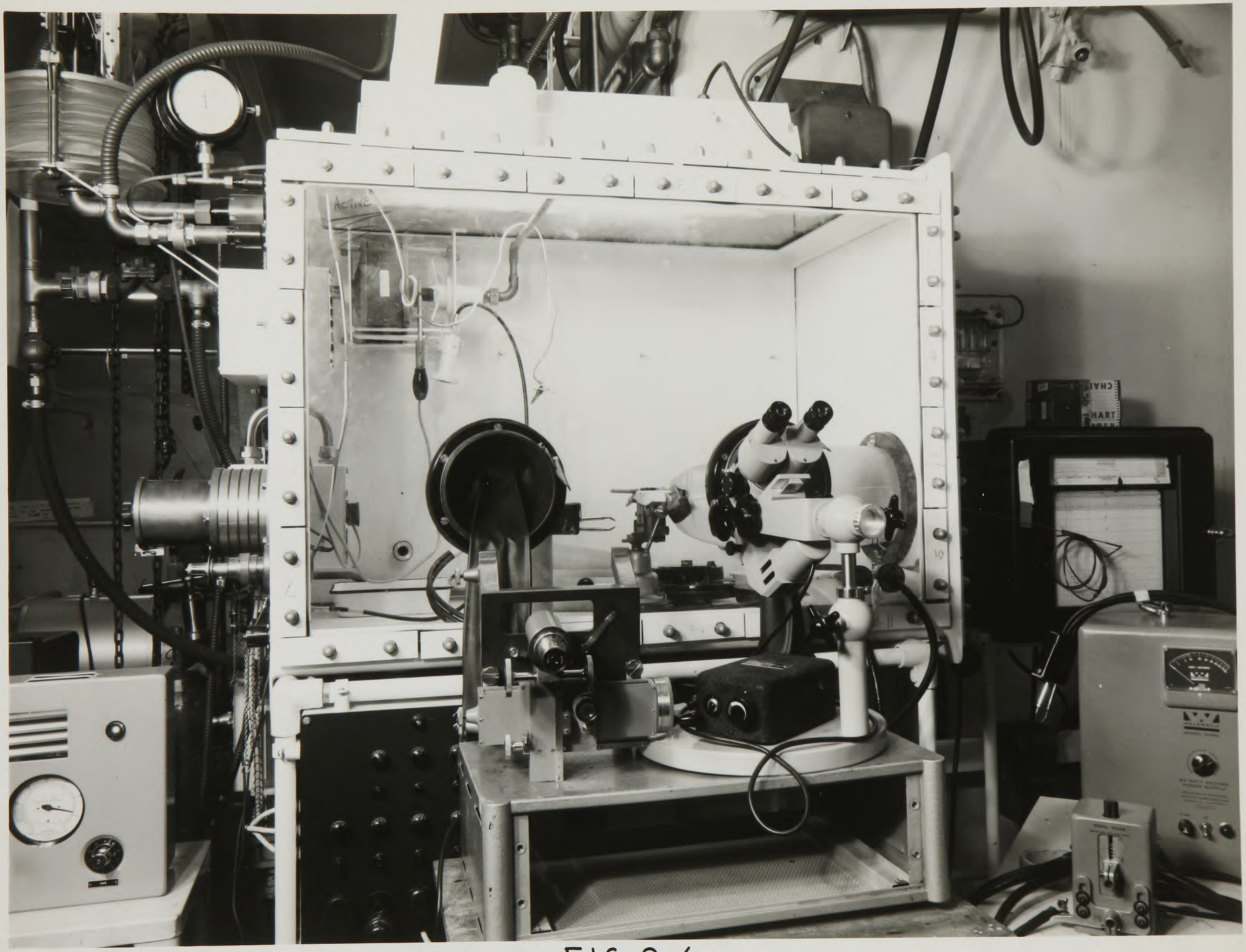


FIG. 2.6.

platinum tube was thus left uncovered so that it could eventually be Woods metalled to the brass capsule. When this bag was attached to the helium filled encapsulation box shown in Fig. 2.6. it was possible to mount the specimen on its platform inside the glove box while most of the seal and its leads remained effectively outside the glove box and free from contamination. In Fig. 2.6. the p.v.c. can be seen entering the glove box from the port on the right hand side of the box. The photograph also shows much of the auxilliary equipment used in mounting the specimens. In the bottom right hand corner is the Weldmatic Model 10260 pressure triggered spot welder power pack, the actual welding tool used being visible just to the left of the vice inside the box. By careful control of the pressure and discharge time it was possible to produce a good weld without blasting away large amounts of the specimen. The high power binocular microscope was used to examine the quality of the spot welded joints and the cathetometer used to measure the potential probe separation. Other equipment visible is that used for maintaining the purity of the helium glove box atmosphere.

Once the specimen had been satisfactorily mounted, the brass capsule was Woods metalled on to the platinum seal as shown in Fig. 2.7. The p.v.c. bag was then withdrawn from the glove box and pulled back over the capsule as shown in Fig. 2.8. Once in this position the p.v.c. bag was thermo-sealed across the black line on the left hand side of Fig. 2.8. Any contamination was thus trapped inside the small p.v.c. bag remaining round the capsule and was not released until the bag was subsequently removed in a fume hood. Decontamination was performed as before by dissolving away the Shellac in methyl alcohol. Occasionally some

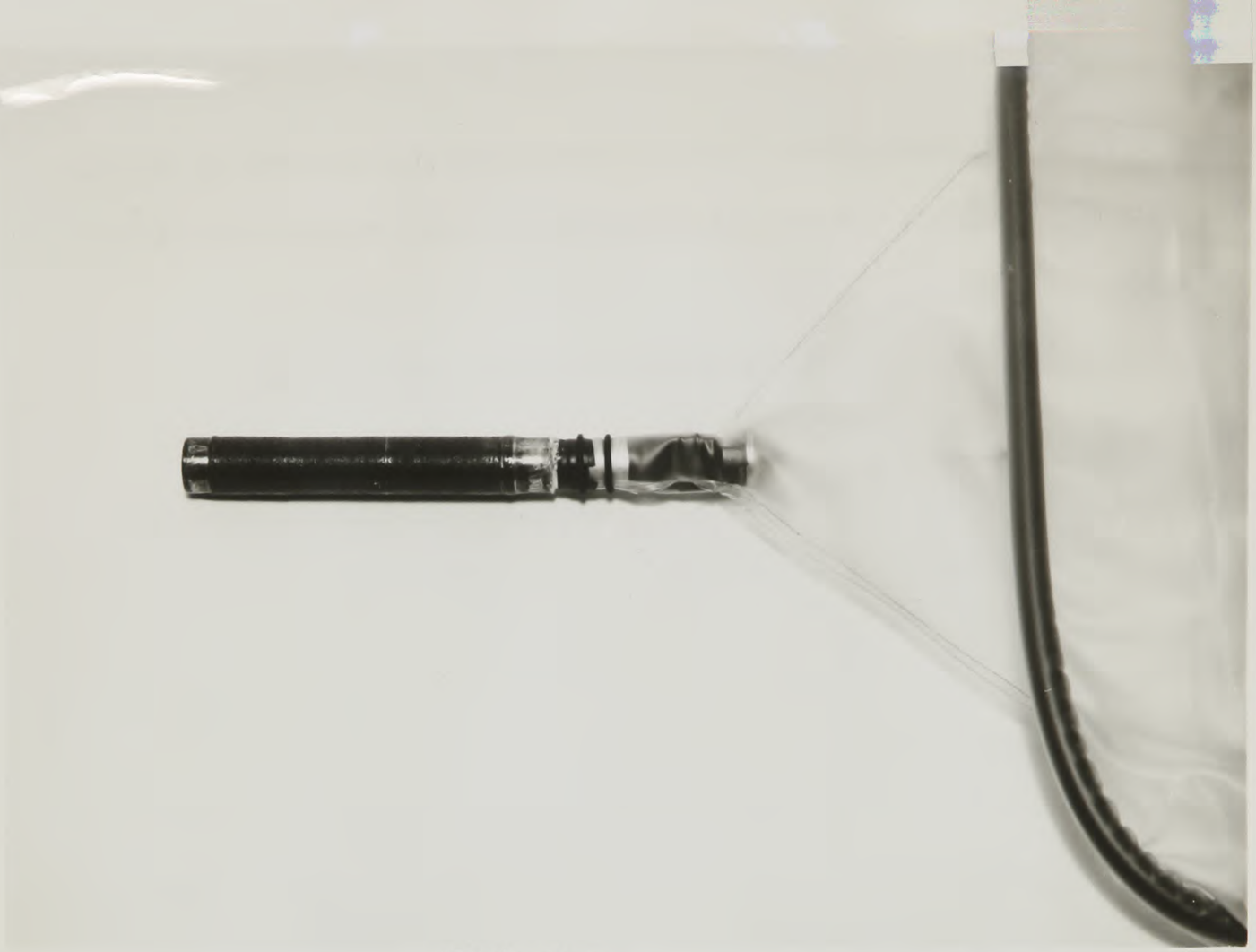


FIG. 2.7.

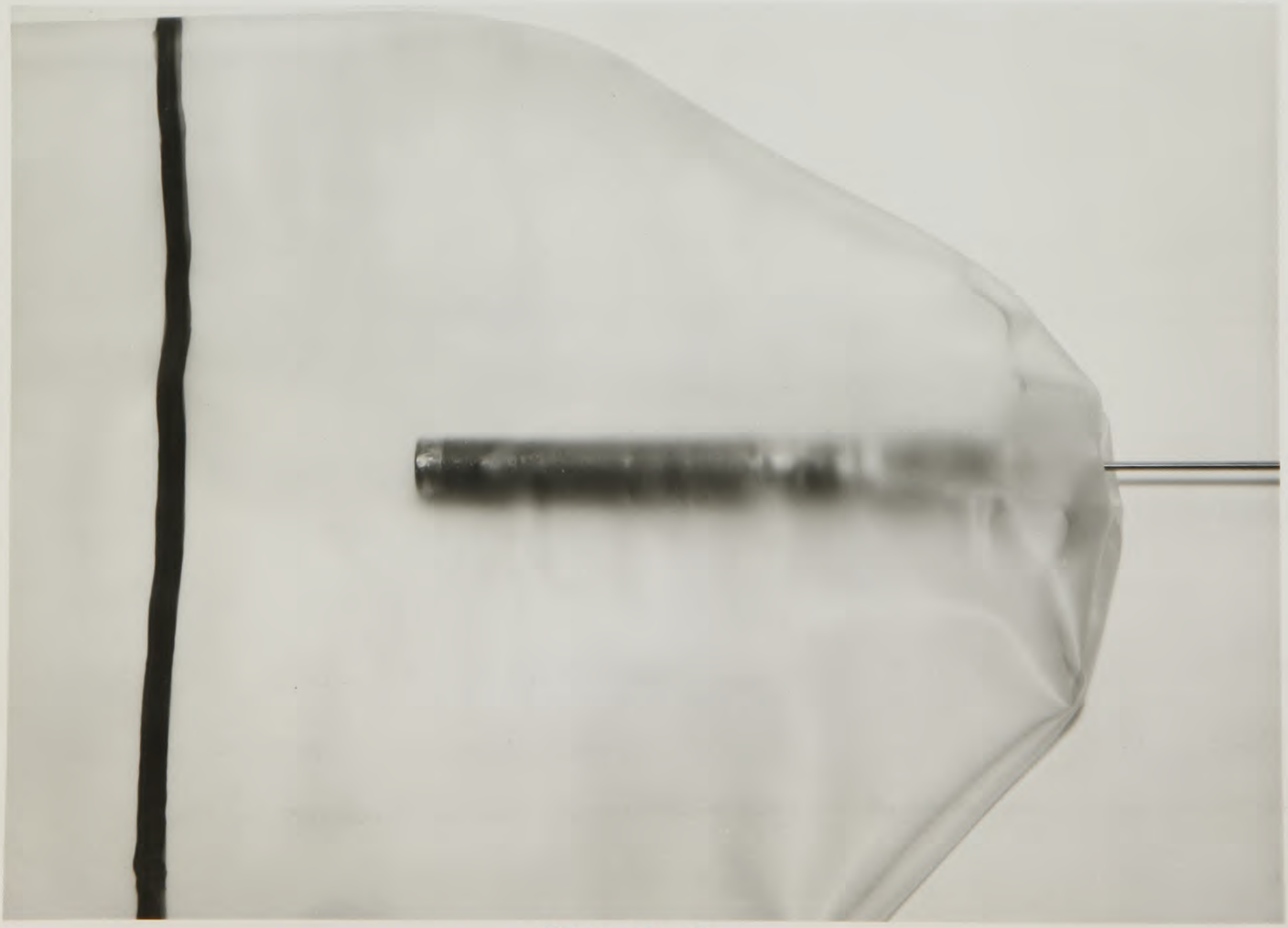


FIG. 2.8.

contamination remained after this treatment and was removed by briefly immersing the seal in dilute hydrochloric acid and vigorously rubbing with a tissue.

Once decontaminated, the sealed capsule was removed to the laboratory and recoated with Shellac to fix any remnant low level contamination. The outer brass case was Woods metalled into position and the wires of the lead harness joined to their respective junctions in the oil bath.

2.5. Cryogenic Holding Arrangements

One of the most important reasons for our choice of sealed capsules in preference to a cryogenic glove box for self-irradiation damage experiments was the extreme ease with which sealed capsules could be held for very long periods at low temperatures. The canned specimens were simply left in 18 litre helium storage dewars whose liquid level was kept above the 3 litre mark by syphoning over more liquid helium from another storage dewar approximately every fortnight. The day to day running of the experiment was greatly helped by the fact that our apparatus was in an "active" building, as it was possible to have the outer jacket of the dewar topped up at frequent intervals every day of the year. We would like to express our gratitude to the men of the "Argon Plant" for carrying out this arduous task.

In Fig. 2.9. we show a photograph of the dewar with two capsules taped to the outside showing their relation to the bottom of the inner vessel. Also visible in the photograph are the oil baths in which the lead harnesses were joined to the multicored cables leading to the measuring system and the thermocouple $0^{\circ}C$ reference junction. It may be

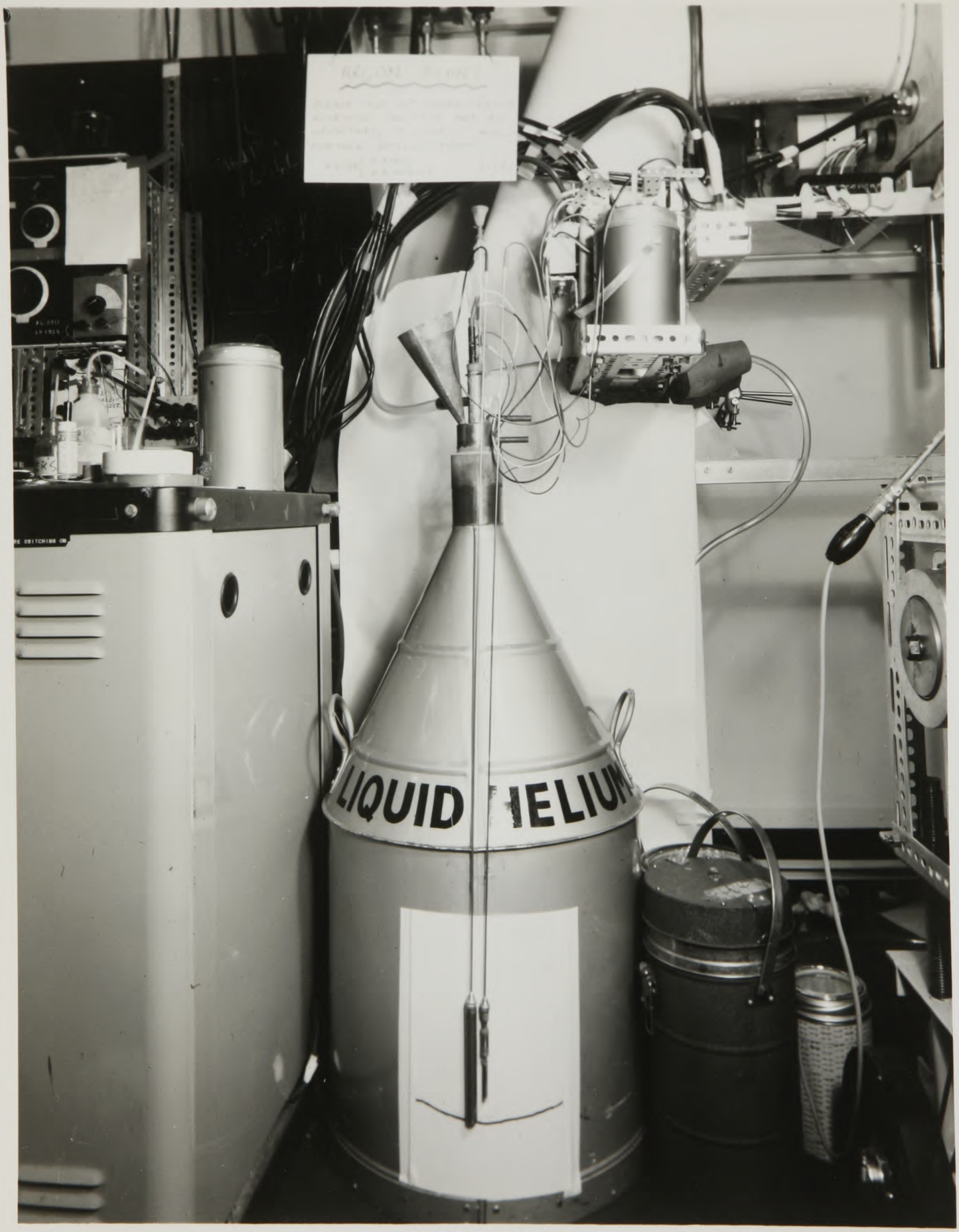


FIG. 2.9.

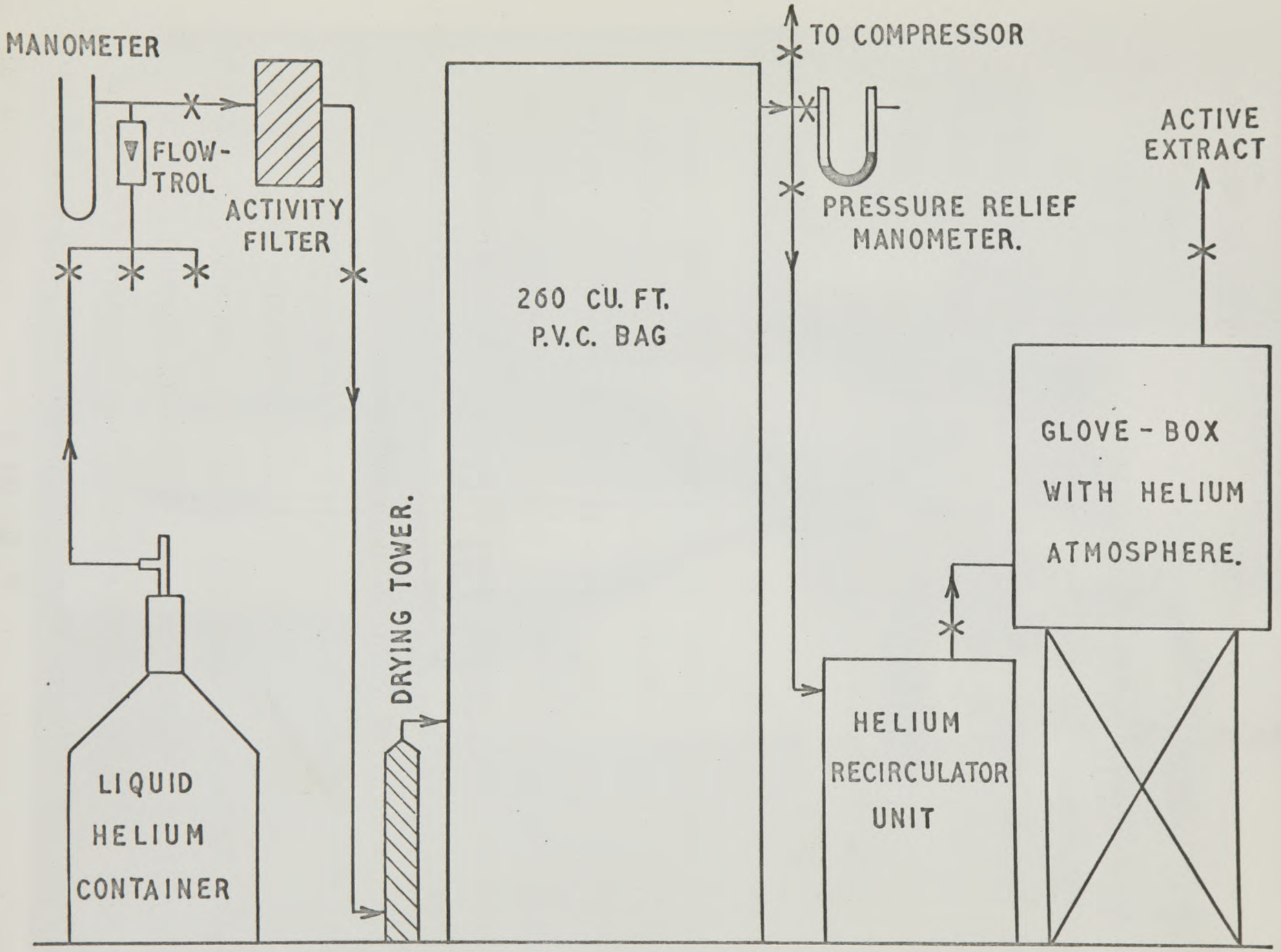


FIG.2.10. BLOCK DIAGRAM OF HELIUM CONSERVATION SYSTEM.

seen that a T piece closes the top of the dewar with a p.v.c. tube leading off from its side arm to the helium return line. The top of this T piece was closed by a rubber cork which was drilled and split to allow the removal of specimens when required and to permit the entry of the transfer syphon. Apart from allowing the collection of the helium gas evolved from the dewar, the system, which ran at a slight overpressure, ensured that no air leaked into the neck of the dewar. Before the return line was fitted air had occasionally solidified in the neck of the dewar making it extremely difficult to introduce or remove the capsules.

A block diagram of the helium conservation system is shown in Fig.2.10. The gas evolved from the dewar passes through a "Flowtrol" gauge and past a methylated spirits manometer which were used to indicate when transfer of liquid helium into the dewar had ceased. While liquid helium was flowing through the transfer syphon a sudden increase in pressure over the liquid in the transfer dewar did not register as a change of pressure in the return line. When however the transfer dewar was empty a change of pressure in the transfer dewar was immediately transmitted to the return line.

By partially filling the pressure relief manometer with oil it was possible to run the return line at a slight bgt constant overpressure and at the same time ensure that the gas bags were continually filled with approximately 260 cubic feet of pure dry helium. This helium gas was used to provide the atmosphere of the glove box in which the specimens were encapsulated. Some hours before a specimen was encapsulated helium gas was drawn off from the p.v.c. bags by the recirculator pump, passed into the glove box and exhausted into the active extract. By thus purging the box atmosphere for a few hours, oxygen impurity contents were reduced to

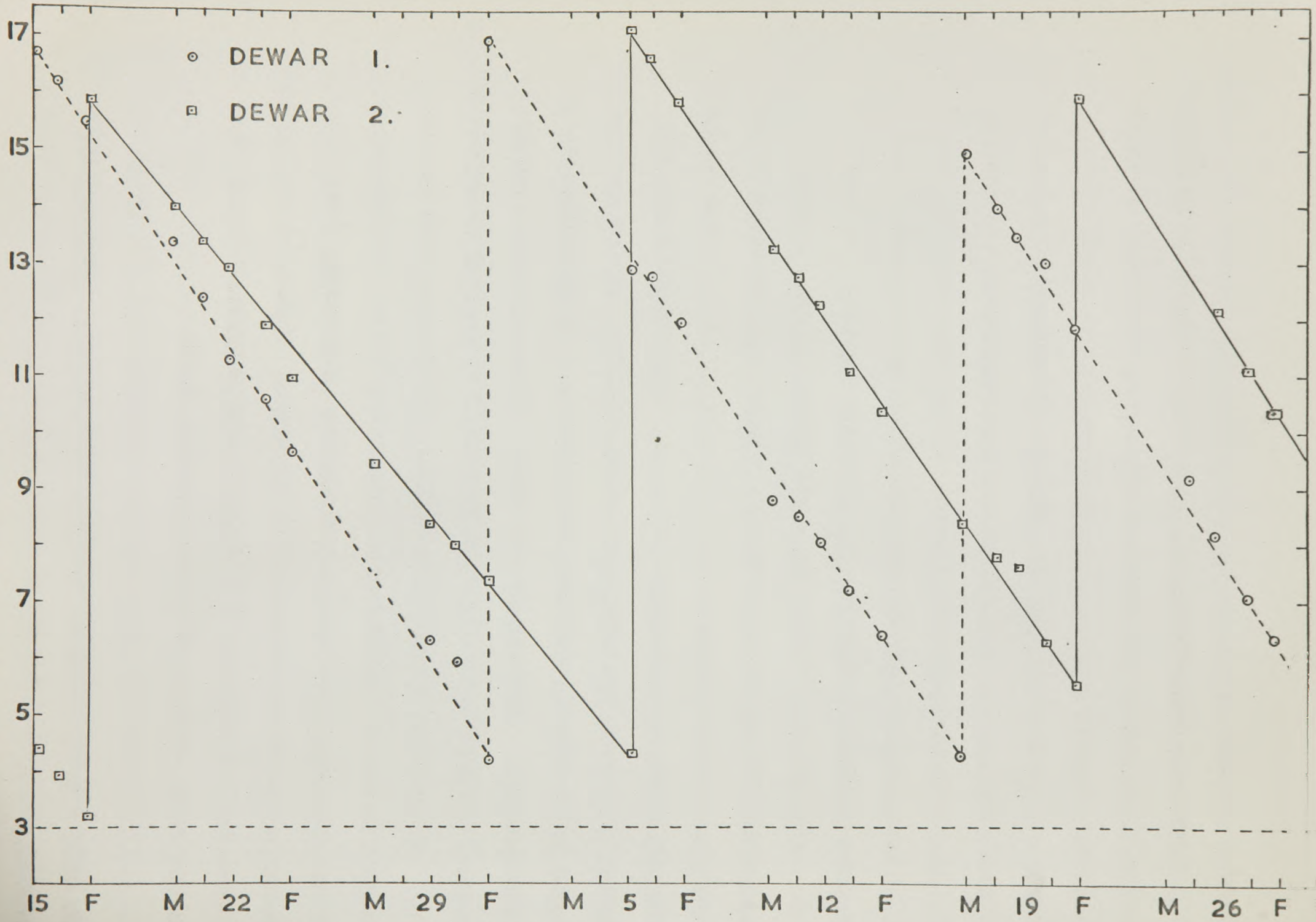


FIG.2.11. LIQUID HELIUM LEVELS MAY-JUNE 1963.

below 1000 p.p.m.*

Finally in this section, Fig. 2.11 shows the variation in liquid level in two helium storage dewars during May and June 1963. The liquid levels were found by using a rubber diaphragm detector of the type described by White (1959) page 58. This was essentially a thin rubber membrane stretched on a 1" diameter cone which tapered down to one end of a long 2 mm. O.D. thin walled German silver tube. When the lower end of the German silver tube was below the surface of the liquid, the helium gas column oscillated spontaneously with a low frequency. On raising the lower end of the tube through the liquid surface, the frequency and amplitude of the vibrations increased. With practice the height of the liquid surface above the bottom of the dewar could be determined to within a few millimeters. Reference to tables supplied by the makers of the dewar allowed these readings to be quickly converted into the volume of liquid helium present. Fig 2.11. shows that the rate of evaporation of liquid helium is independent of its level. This property was extremely useful as it allowed us to predict when the level was going to fall below the 3 litre mark we set as a safe minimum. If this was going to occur during a weekend or holiday period steps were taken to refill the dewar beforehand and so prevent the accidental warm up of valuable irradiated specimens. As already mentioned the increase in evaporation rate of dewar 2 from .61$_3$ litres/day prior to June 5th to .740 litres/day after June 5th was due to the addition of another specimen, Pu.12.

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*We would like to record our gratitude to R.O.A. Hall (A.E.R.E.) for constructing this helium canning box for our use.

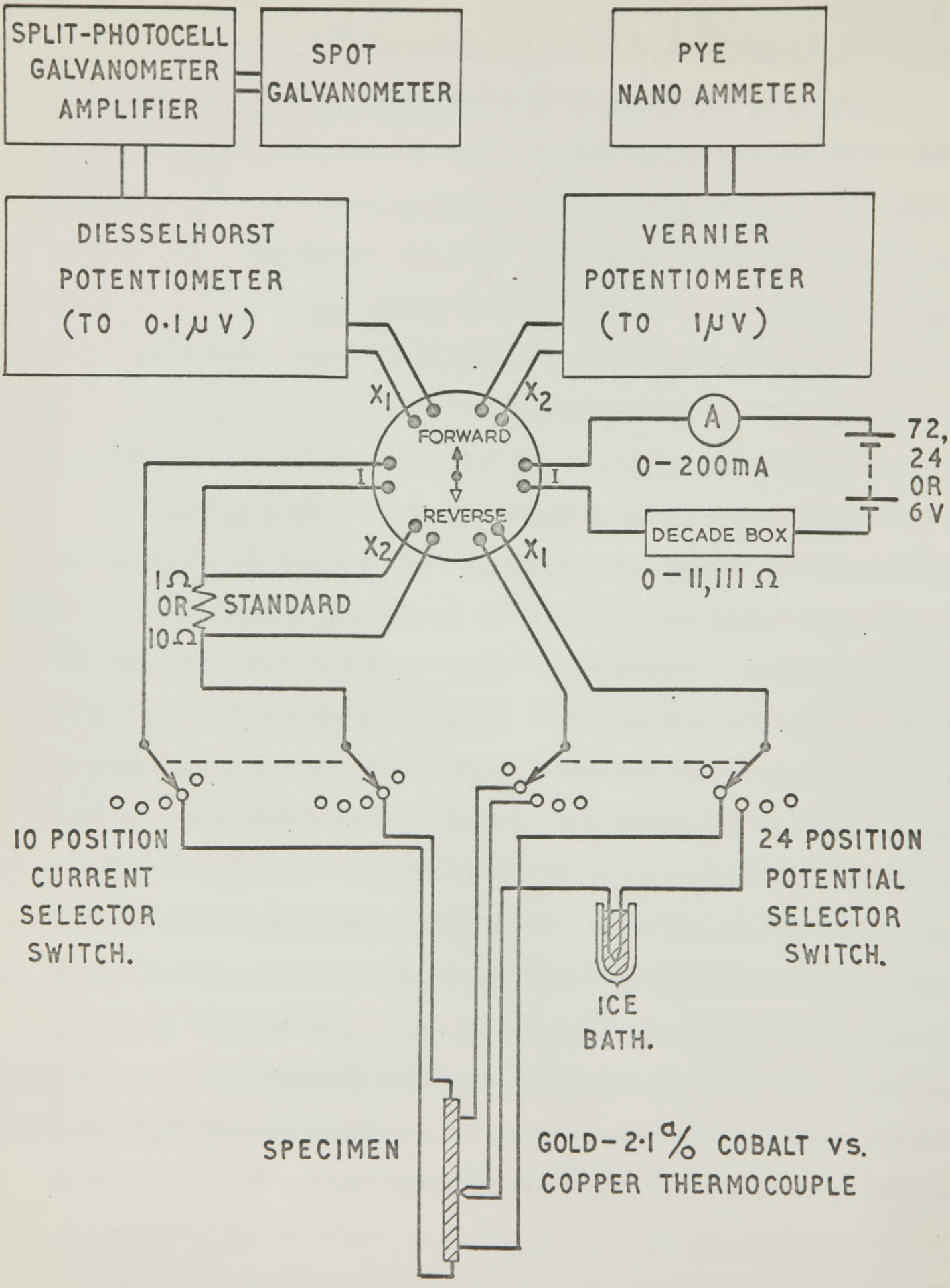


FIG.2.12. BASIC MEASURING CIRCUIT.

2.6. The Measurement of Electrical Resistance

The three main requirements which must be fulfilled by any system used to measure the electrical resistances of specimens undergoing self-irradiation damage are that it should:

i/ Be sensitive enough to measure a change of about 10^{-6} ohms in a resistance of the order of 10^{-2} to 10^{-5} ohms;

ii/ Be virtually free from both long and short term drift;

iii/ Be easily and quickly operated.

The measuring system evolved by us to meet these requirements was based on a Diesselhorst potentiometer and is shown in Fig. 2.12. The specimen was mounted as a 4 terminal resistor and the potential developed across it was compared with that developed across a 1 or 10Ω standard resistor connected in series with the specimen. In order to avoid frequent resetting of the dials the voltages developed across the specimen and standard resistor were measured on separate potentiometers. The Diesselhorst potentiometer, with a Tinsley type 5214 split-photocell galvanometer amplifier acting as a sensitive null detector was used to measure the voltages developed across the specimen and a Cambridge Vernier potentiometer, with a Pye Nanoammeter as null detector, used to measure the voltage across the standard resistor. Elimination of parasitic thermal e.m.f's developed in circuit was made possible by the inclusion of a Tinsley thermoelectric-free reversing switch which enabled the polarity of its three inputs to be simultaneously reversed. The current source was connected via one input, the voltage developed by the specimen via the second and the voltage developed across the standard resistor via the third. In this way the polarity of the voltage seen by the two potentiometers remained unchanged when the direction of the current was

reversed. By averaging the readings obtained before and after current reversal, the unipolar thermal e.m.f's could be eliminated.

As the potentials from up to twelve separate specimens were to be measured within as short a time as possible, selector switches were included in the measuring circuit. The selector switch included in the "current" circuit was an ordinary double pole rotary wafer type, thermal e.m.f's being considered unimportant. As the "potential" measuring circuit was handling voltages which were to be measured to better than $^1/_{10}$ V, a Tinsley 24 channel all copper selector switch was used in this circuit. It was mounted in a screened metal box filled with transformer oil to reduce the magnitude of thermal e.m.f's generated during switching. Repeated switching between channels failed to develop parasitic voltages greater than 10^{-8}V.

The specimen current was obtained from twelve 6 volt, 60 amp.hour, car batteries connected in series to give a 72 volt D.C. source. A decade resistance box connected in series with the batteries and the specimen enabled a measuring current of 100 mA to flow in a circuit of total resistance ~ 720 ohms. After coarse adjustment of the circuit resistance to give approximately 100 mA as shown by the milliammeter, fine adjustment of the circuit resistance gave a current of 100.000 mA indicated by a voltage of 0.100000 developed across the 1Ω standard resistor and measured on the Cambridge potentiometer. In fact a rough calculation will show that as the smallest available increment of resistance was $^1/_{10}\Omega$, the corresponding incremental change in current was 13μA. The current obtained from the batteries connected in this circuit was however found to decay steadily under normal conditions at

a rate of ~ 50μA/minute. Thus it was possible to obtain a current of exactly 100.000mA about 4 times per minute. By prior balancing of the Diesselhorst potentiometer it was possible to measure the potential developed across the specimen for a current of exactly 100.000 mA when their respective null detectors showed that both potentiometers were simultaneously balanced. The batteries were recharged when, or rather before, the rate of current decay became unmanageably rapid. The outstanding advantage of this type of measurement was that the voltages developed across the specimen could be mentally changed into resistances without the laborious calculation involved in, say, dividing a potential of 2638.6$_5$ μV by a current of 100.010 mA to get a resistance of 26.383 mΩ .

2.6i. Probable Accuracy and Reproducibility of Resistance Measurements

The smallest increments available on the dials of a Diesselhorst potentiometer are $^1/_{10}$ μV; interpolation between these increments is however possible with a sensitive null detector. Table 2.B. shows the sensitivity of the type 5214 split photocell galvanometer amplifier, when used with the recommended type 552-45E indicating galvanometer, as a function of the circuit resistance. With a typical circuit resistance of ~180Ω the galvanometer spot deflection of 8.8 mm/$^1/_{10}$ μV allowed the detection of a change in voltage of $^1/_{100}$ μV (10^{-8}volts). In practice readings were never taken to better than 0 or 5 x 10^{-8}volts.

For Table 2.B. see over...

TABLE 2.B.

Deflection of galvanometer spot in mm. for an applied potential of $^1/_{10}$ μV with the amplifier at maximum gain. Tinsley type 5214 amplifier and type 552-45K galvanometer

Resistance (ohms)	Deflection (mm.)	Resistance (ohms)	Deflection (mm.)
1	74	80	16
5	63	100	14
10	54	140	10.6
15	50	180	8.8
20	43	200	7.9
30	32	300	5.5
40	26	400	4.1
60	20		

The Cambridge Vernier potentiometer with a Pye nanoammeter as its null detector was capable of detecting a change of 1 μV and hence a change of 1 μA passing through the 1 Ω standard resistor. The current of 100 mA could therefore be quoted to the 5th figure if the standard resistor was invariant with temperature and time. No correction was applied for the small temperature coefficient of resistance of the standard resistor in view of the large amount of work this would have involved. In order to see what effect was caused by this neglect we analysed the resistivity versus time curve for αFe.5 from 5000 to 6000 hours. The standard deviation of the readings from a smooth curve was 0.01%, which in fact meant an error of $\sim^2/_{10}$ μV in a reading of ~ 2,000 μV. Thus the long term reproducibility of these resistivity measurements must be limited to about 1 part in 10^4. No correlations between the deviations

from a smooth curve and the temperature of the standard resistor were found and it would appear that our neglect of the temperature coefficient of the standard resistor was justified.

2.7. Temperature Measurements

The majority of our self-irradiation experiments were carried out with the specimens immersed in one or other of the common cryogenic liquids and it was assumed that the temperature of the specimen was virtually that of the liquid bath. For the determination of intermediate temperatures one junction of a Gold-2.1 At.% Cobalt versus Copper thermocouple was placed on, or as near as possible to, the specimen, and the other junction held in a bath of crushed melting ice. The choice of this particular thermocouple pair was dictated by the need to have as large a thermoelectric power as possible at the lowest temperatures; the thermoelectric power of this thermocouple pair being still ~ 4 μV/ $^{\circ}$K at 4°K compared with ~ 20 μV/$^{\circ}$K at 20°K and ~ 40 μV/ $^{\circ}$K at room temperature. Calibration tables for Gold - 2.1 At.% Cobalt versus Copper thermocouples have been given by Powell, Bunch and Corruccini (1961) (hereafter P.B. & C.) and were used by us as a basis for the calibration of our thermocouples. Our Gold - Cobalt wire was obtained from Johnson Mathey and Co. and the copper was from a reel obtained from Oxford. As a thermocouple pair they gave readings consistently lower than P.B. & C., ~ 9400 μV w.r.t. 0°C for the helium point, for example, compared with 9852 μV quoted by P.B. &C. As we had no alternative but to use the wire available the following calibration procedure was used:

i. The e.m.f. of the thermocouple was measured w.r.t. 0°C at the

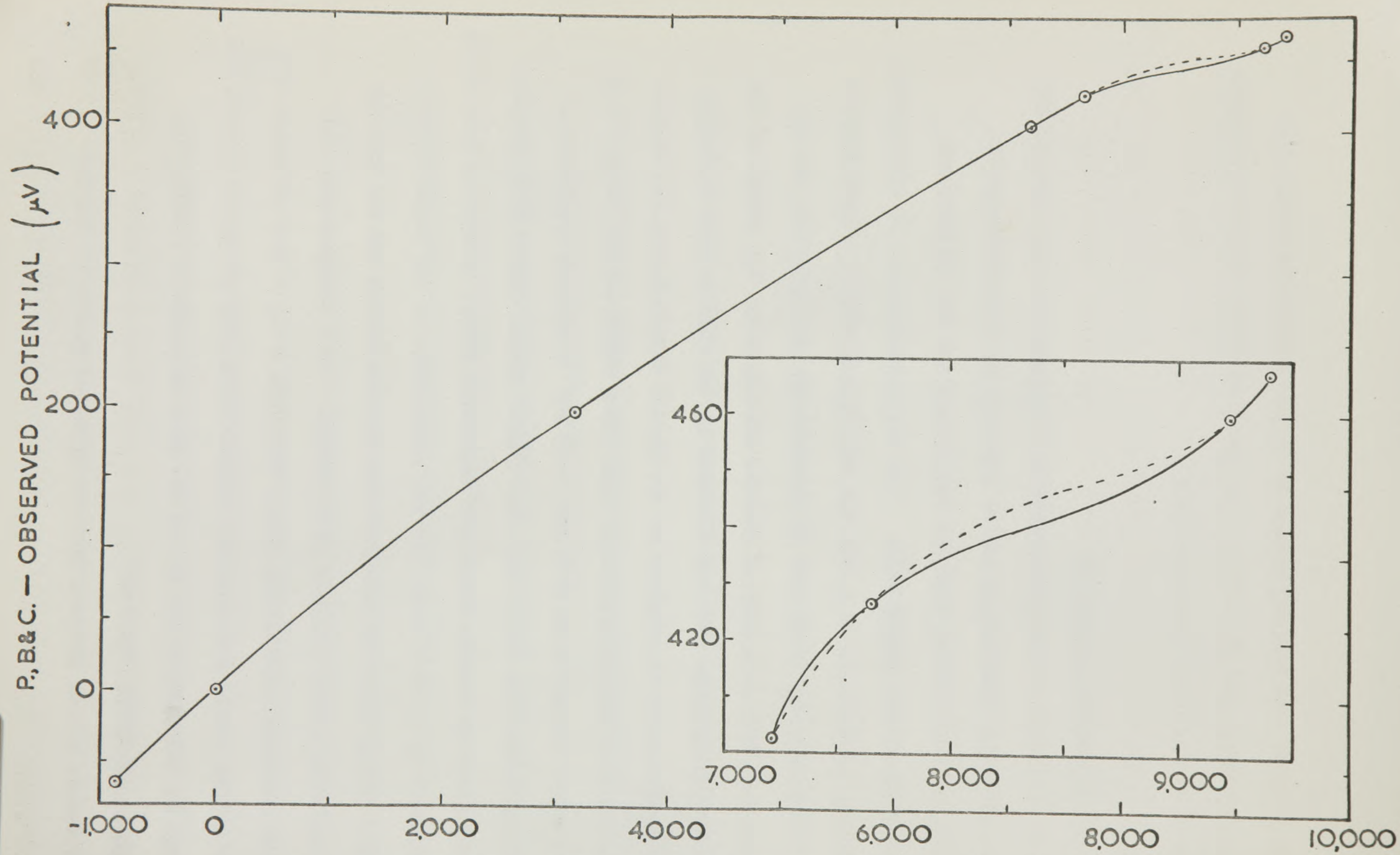


FIG. 2.13. CALIBRATION OF WHITE THERMOCOUPLE

following points: the boiling points of liquid helium, hydrogen, nitrogen and oxygen and the sublimation point of carbon dioxide in Ether.

ii. These values were subtracted from the appropriate values given by P.B. & C. to give the difference between our reading and that of P.B. &C.

iii. This difference was plotted against our observed value as shown in Fig. 2.13 and the points were joined with as smooth a curve as possible. It was assumed that this smooth curve gave the difference between our observed e.m.f. and the appropriate P.B. & C. value for temperatures between our measured values.

iv. At any intermediate value of the observed e.m.f. the difference obtained from Fig. 2.13 was added to the observed value to give the equivalent P.B. &C. e.m.f. Reference to the tables of P.B. & C. enabled the corresponding temperature to be obtained.

v. A graph similar to that shown in Fig. 2.14 was constructed from as many points, obtained as described above, as were required to define a smooth curve. In fact more than one such graph was constructed for each thermocouple, the larger scale and hence the more accurate plots being made for those temperature regions of major interest, usually $\sim 5^{\circ}K$ to $\sim 50^{\circ}K$.

Returning now to Fig. 2.13 it can be seen that the major criticism which can be levelled at this calibration procedure is the highly arbitrary nature of the curve joining the measured points. This is especially so in the interval between the boiling points of liquid nitrogen and liquid hydrogen; the inset of Fig. 2.13 shows two such possible curves. The solid line was the one used in the subsequent determination of Fig. 2.14. The maximum deviation between the two curves shown in the inset is $\sim 5\ \mu V$ at temperatures where the thermoelectric power is $\sim 30\ \mu V/^{\circ}K$ and so the

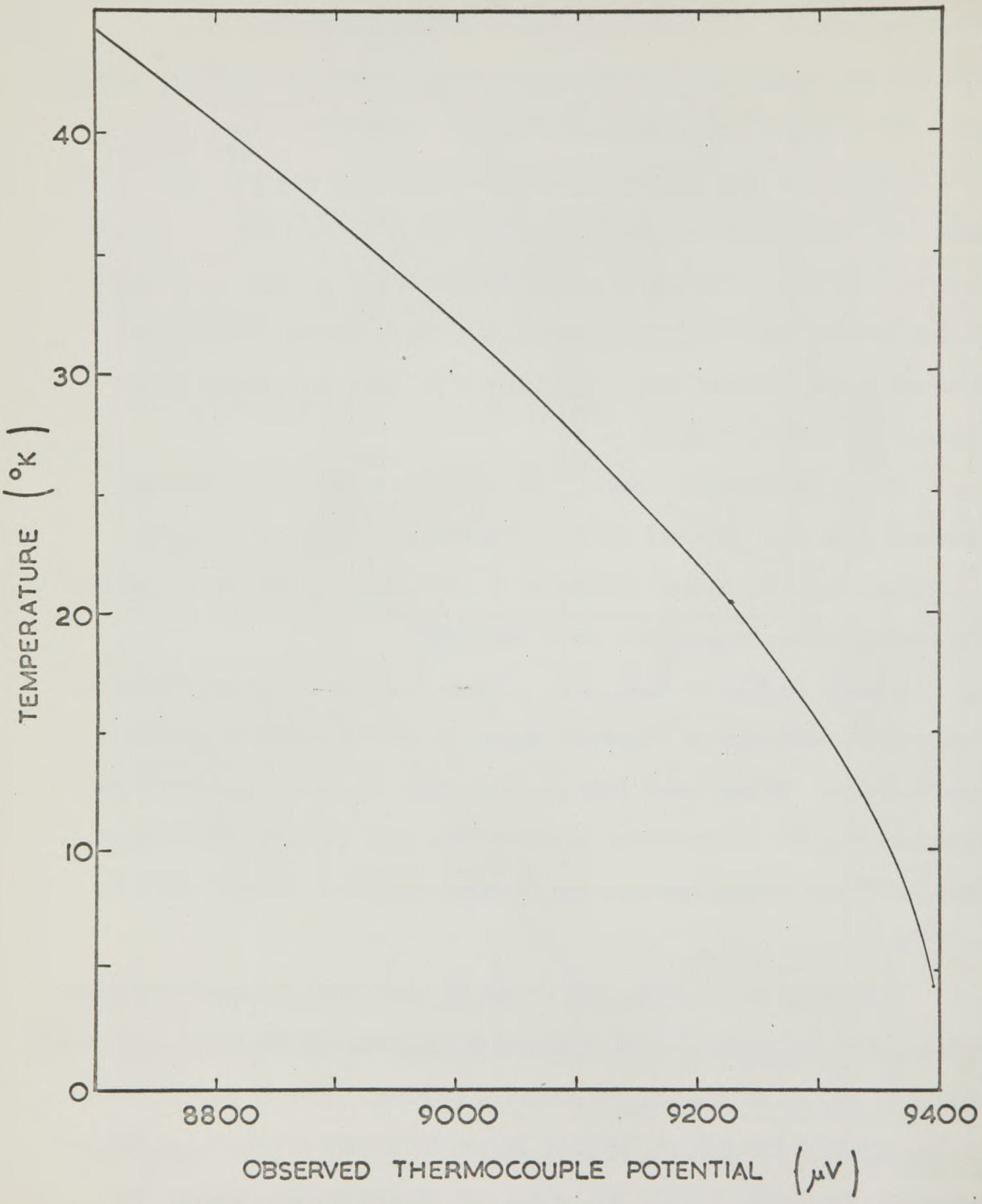


FIG. 2.14. CALIBRATION OF WHITE THERMOCOUPLE

maximum systematic error introduced in this way should not be more than $\sim 0.25^{\circ}K$.

In order to achieve a better calibration than obtained in this manner we ordered a Tinsley low temperature platinum resistance thermometer which was calibrated at the N.P.L. between $12^{\circ}K$ and $300^{\circ}K$. However this thermometer did not arrive until after our experimental work ceased and it was not possible to check even the fundamental shape of the curve of Fig. 2.13.

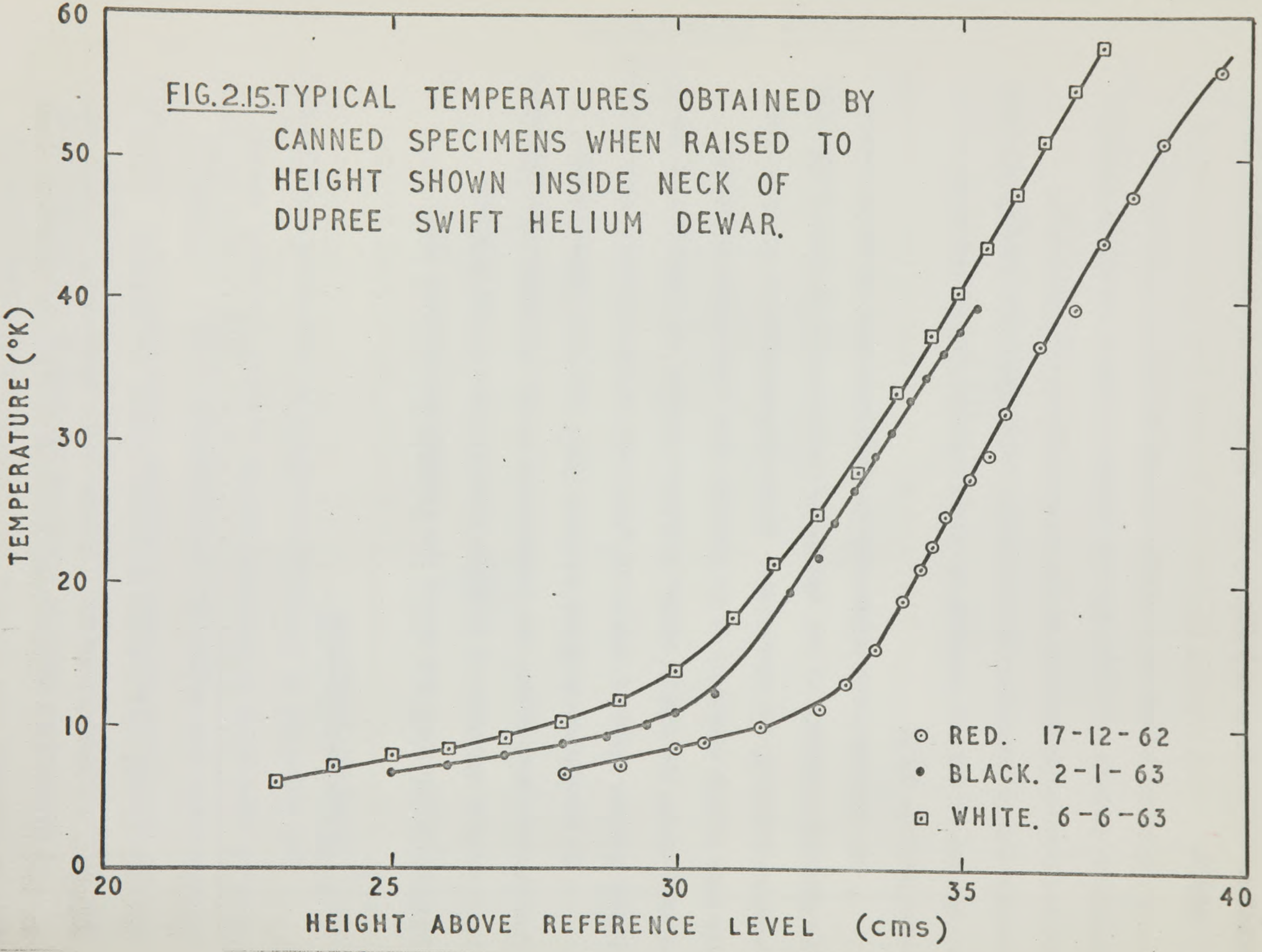
One further point which must be considered when trying to assess the probable accuracy of our temperature measurements is that of the self heat generated by the specimens. Since this amounted to up to ~ 5 mW for some of our specimens it is probable that temperature gradients existed along the length of our specimens despite the inclusion of the fairly massive piece of copper on which most of the specimens were mounted.

In conclusion we would consider that, with due regard to the factors mentioned above, the temperatures of our specimens were determined to an overall accuracy of $\pm 0.5^{\circ}K$, although for any one specimen reproducibility from run to run was probably better than this.

2.8. Annealing Techniques

The technique of Isochronal annealing of self-irradiated specimens was often used by us to establish details of their annealing spectra. Experimentally this called for the ability to maintain temperatures constant for periods of about 30 minutes. Various methods of doing this were tried, the two most successful of which are described below.

A temperature gradient exists in the neck of any liquid helium storage dewar and this property was utilised for the maintenance of


FIG. 2.15. TYPICAL TEMPERATURES OBTAINED BY CANNED SPECIMENS WHEN RAISED TO HEIGHT SHOWN INSIDE NECK OF DUPREE SWIFT HELIUM DEWAR.
TEMPERATURE (°K)
0
10
20
30
40
50
60
20
25
30
35
40
HEIGHT ABOVE REFERENCE LEVEL (cms)
RED. 17-12-62
BLACK. 2-1-63
WHITE. 6-6-63

constant temperatures notably up to ~ 80°K, but on occasions up to ~ 180°K. When held at any point in the neck of a storage dewar, a canned specimen of the type used by us will eventually reach an equilibrium temperature determined by the net effect of the heating due to Joule and self heat and the cooling due to radiation from the inside of the neck of the dewar and conduction from the cold helium gas passing up the neck of the dewar. This mean temperature was found to vary according to the position of the specimen in the neck as shown in Fig.2.15. It can be seen that the temperature gradient becomes much steeper at heights of about 30 cm. from the bottom of the dewar, this being the height at which the dewar narrows from the spherical helium container to the cylindrical neck. For the determination of resistivity-temperature curves of the type to be shown in Figs. 3.5. and 3.6., the time required for a specimen to reach its equilibrium temperature was unimportant. However for Isochronal annealing experiments it was important that the desired temperature should be reached as rapidly as possible. This could be done once the approximate equilibrium position was known. By increasing the current through the specimen to ~150 mA, the maximum allowed by the lead insulation, and by raising the specimen to a few centimeters above its eventual equilibrium position, an initial fast rise in temperature could be achieved. As the temperature approached its required value, the specimen was lowered to its final position and the current passing through it was reduced. A constant temperature was achieved by varying the Joule heat developed by the specimen, and/or by adjusting the position of the specimen in the dewar neck. With practice it was possible to hold temperatures constant in this way to within about ± 0.25°K.

Attempts were also made to construct automatic annealing cryostats in which the heat leak to a bath at a lower temperature was balanced by the heat generated by a heater wound round the specimen. This balance was to be controlled by a servomechanism operated by the output of a thermocouple biased to give the required temperature. No reliable cryostats of this type were, however, developed, mainly because of the large time constant of the feedback system used.

The method used to obtain steady temperatures in the range between the boiling point of liquid oxygen and room temperature relied on the latent heat of fusion of a range of organic liquids. A list of these liquids, together with their approximate melting points and some comments as to their suitability for cryogenic use are given in Table 2.C.

TABLE 2.C.

Substance	Freezing Point °K	Freezing Point °C	Suitability for cryogenic use
Isopentane	114	-159	Viscous but irreplaceable
Ether	150	-123	Very good
Ethyl Bromide	154	-119	Reasonable
Ethyl Alcohol	158	-115	Viscous. Not good
Carbon Disulphide	163	-110	Smell !
Methyl Acetate	172	-101	Good
Acetone	178	-95	Very good
Methyl Alcohol	178	-95	Viscous. Not good
Ethyl Acetate	189.5	-83.5	Good
Carbon Dioxide (+Acetone)	194.5	-78.5	Standard point
Cymene	199.5	-73.5	Smell !
2 Chloro Ethanol	204	-69	Harmful vapour
Chloroform	209.5	-63.5	Good
m.-Xylene	249	-54	Reasonable
Pyridine	234	-42	Smell !
Diethylamine	233	-40	Smell !
Carbon Tetrachloride	250	-23	Good

Liquids were chosen because of the ease with which they could be handled and stored at room temperature, compared with the difficulty in liquifying gases not usually available in liquid form.

The liquid to be used for a freezing bath was placed in the inner of two small concentric dewars and small quantities of liquid nitrogen were added to reduce its temperature. By careful addition of liquid nitrogen and constant stirring of the liquid it was possible to obtain a constant temperature bath of melting solid. Certain liquids, methyl alcohol for example, do not freeze conveniently at one temperature but gradually become more and more viscous as the temperature is lowered until they eventually solidify. Such liquids do not produce good freezing baths and are best avoided if possible. Other liquids are unsuitable because of their vile odours and/or harmful vapours. Most of the liquids listed are inflammable and have to be handled carefully.

We recommend that rubber gloves and full face shields or gas masks should be worn when using these freezing liquid baths, and that, if possible, the operation should be carried out in a fume hood or under extract.

One obvious drawback of this method is that not every temperature range can be completely covered in this way due to the unobtainability of convenient liquids. The liquids used by us were those obtainable with ease from the A.E.R.E. stores. A list of organic and inorganic substances indexed by the temperature of their freezing point is printed on pages 1325 ff. of the "Handbook of Chemistry and Physics", 44th Edn. (The Chemical Rubber Publishing Co.). A diligent search among these pages will usually produce some substance with the required freezing

point. This does not however guarantee that the substance is easily obtainable.

2.9. Specimen Preparation

In the course of the experiments described in this thesis we have used ten specimens of α plutonium two of δ stabilised plutonium and one each of neptunium and uranium 233. Details of these specimens are given in Appendix I. The initial arc melting and billet casting were carried out in an argon arc furnace and the billets subsequently either machined to the required dimensions or extruded into wire form. We would like to record our indebtedness to the many people who carried out these operations. As a general rule it was found that the machined specimens had more accurate form factors, but gave smaller signals, than the extruded specimens. As, in most cases, we were more interested in the accurate determination of changes in resistance than in knowledge of the absolute resistivity, the majority of our specimens were of extruded wire. The specimen densities were determined by using the displacement method with ethylene dibromide as the fluid. The accuracy of the density so determined depended on the size of the specimen and was typically $\pm$ 0.15%. The form factors of the specimens were usually determined by measuring the specimen diameters with a micrometer and the potential probe separations with a cathetometer. However some specimens were found to have diameters which varied by as much as a few percent along their length or around their girth. In order to minimise the error introduced into the form factor by these variations of diameter, an independent method was used to determine the cross sectional area of these specimens. Having found the mass and density of the specimen by

weighing it was possible to calculate its volume. If the specimen was nearly straight and had reasonably "square" ends, division of the volume by the length gave the mean cross sectional area. This value we consider was more accurate than that obtained by arithmetic averaging of a number of diameters taken along the length and around the girth of a specimen. The room temperature resistivity of the majority of our specimens was also determined by using a knife edge jig developed by F. King. This removed the errors involved in measuring the potential probe separation by determining the resistance between two knife edges of known separation. The form factors used in converting our resistance measurements into resistivities were corrected if necessary to give agreement between the resistances obtained by these two methods. We would put the resultant error in the absolute value of the resistivity of our specimens as $\lesssim 1\%$ unless otherwise stated.

CHAPTER 3 *

The Increase in Resistivity of Alpha Plutonium during Self-Irradiation at Low Temperatures

3.1. Basic Results

The nucleus of Pu. 239 has a half life with respect to α disintegration of 24,360 years resulting in the decay of approximately 2.2×10^9 atoms per gm. per second. The energy released per α disintegration is about 5.3 Mev. and appears as the kinetic energy of the α particle and the recoil U. 235 nucleus. As the range of an particle in plutonium is $\sim$ 500 A° and the range of the U. 235 recoil about 60 A°, these figures having been given by Vinyard (Elliott, Olsen and Vinyard (1963)), the majority of the decay products come to rest inside the metal in interstitial or substitutional positions. Their kinetic energy is transferred to the lattice atoms by collision and appears eventually in the form of heat. For pure Pu. 239 this self heat amounts to 1.90 mW/gm but as the available plutonium always contains the heavier Isotopes Pu. 240, Pu. 241 and Pu. 242 as well as Pu. 238 and Am. 241, the self heats range from $\sim$ 2.1 to $\sim$2.9 mW/gm, depending on the actual Isotopic content. Some idea of the consequences of this high rate of self heating may be obtained from the fact that a 50 gm mass ($\sim 2\frac{1}{2}$ cc.) of metal will maintain itself at a temperature 10° C or

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* Part of the subject matter of this chapter has been published in papers by Lee, J.A., Mendelssohn, K., and Wigley, D.A., Cryogenics 2 183 (1962) and Physics Letters 1 325 (1962)

so greater than its surroundings if these are solely gaseous. As far as the effect of its α -disintegration on the physical properties are concerned, Dempsey and Kay (1958) have calculated that periods of at least a century would be necessary before the accumulation of helium produced any appreciable change in the physical properties at room temperature. Similarly Meaden (Thesis, 1961) states that he found no change in the residual resistance of one of his plutonium samples when it was re-measured after an interval of one year stored at room temperature.

In October, 1964 Olsen and Elliott (1964) reported that they had found that the resistivity of plutonium increased as a linear function of time when held at low temperatures. The rates of resistivity increase when held at 4.5°, 20.1°, 64.7° and 77.1°K were 0.0641, 0.0658, 0.0038 and 0.0014 $\mu\Omega$ cm/hr respectively. At the same meeting Bonnerup reported that his specific heat results showed that the energy released from specimens which had self damaged at 20°K caused a decrease in the measured specific heat between 60 and 100°K, the magnitude of the decrease being proportional to the length of time held at 20°K. Meaden (priv. comm.) states that he too had noticed a slight rise in the resistivity of one of his specimens during the course of an 8 hour run at or below 4.2°K, but that with the cryostat used it was impossible to obtain longer holding times and he was unable to follow up this observation.

In order to check some of these interesting results we encapsulated sample Pu.1, a rod of medium purity α plutonium, details of which are given in Appendix I. Current and potential leads were attached to the specimen and it was hung from a thread inside a 15 litre Dupree Swift

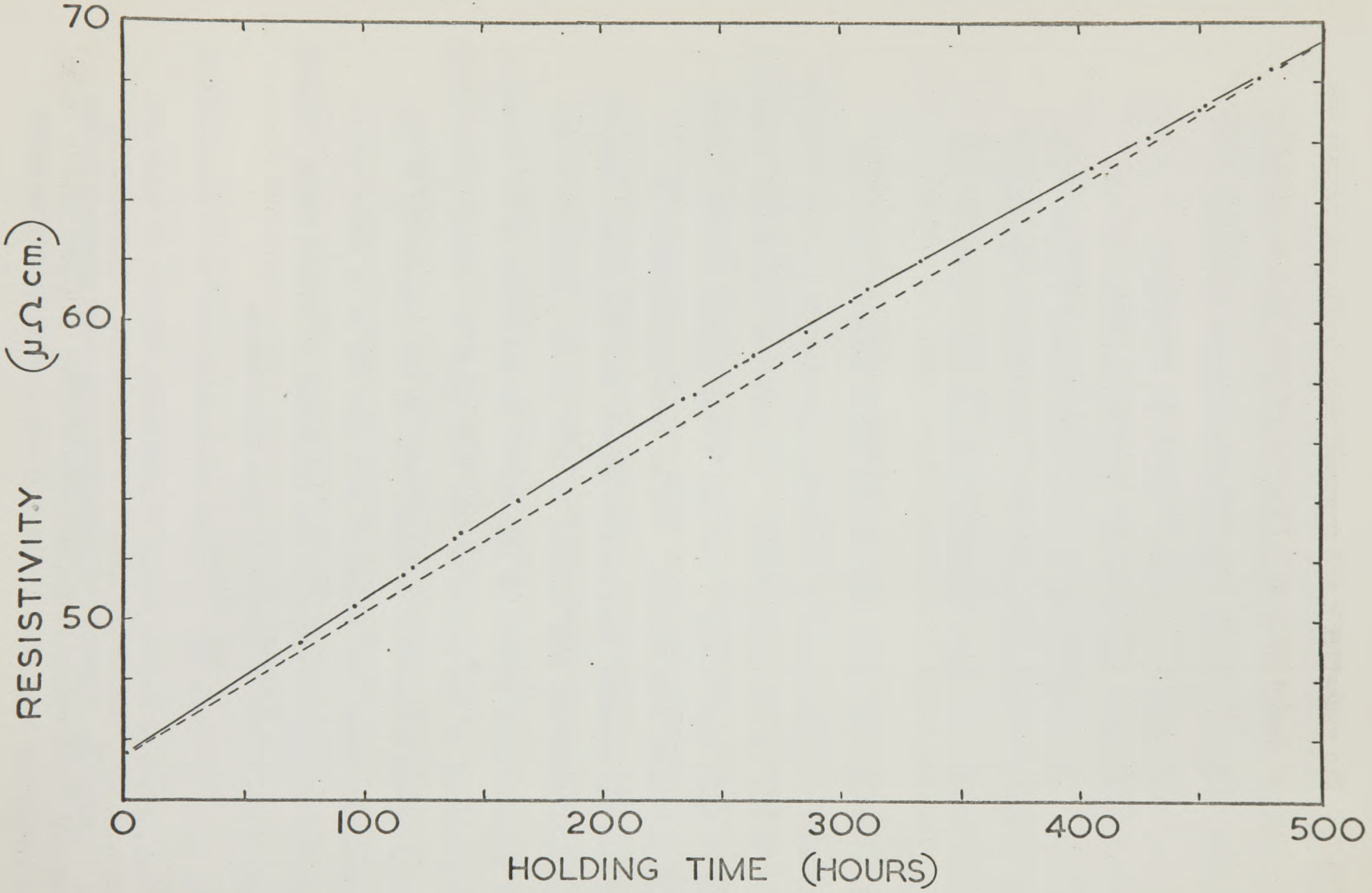


FIG. 3.1. Pu1 FIRST HOLDING RUN IN LIQUID HELIUM NOV.-DEC. 1961

helium dewar. Its resistivity was measured about twice per day and the resultant graph of resistivity as a function of time held in helium is shown in Fig. 3.1. It can be seen that the rate of resistivity increase decreased with time to about 83% of its initial rate after ~ 450 hours at ~ 5°K, a feature not evident from the American work. Our initial rate of resistivity increase, 0.091 $\mu\Omega$ cm. was lower than the value of 0.064 reported by Olsen et al.; this was later found to be due to the difference in purity and isotopic content of the specimens used. After about 490 hours the helium level in the Dupree Swift fell undesirably low and as we were unable at that time to transfer liquid helium between storage dewars, the run was abandoned.

A few weeks later three other samples, Pu. 2, 3 and 4, were encapsulated and were mounted ready for further self-irradiation damage experiments. The electrical leads to the specimen were protected by passing them inside German silver tubes and the capsules themselves were protected by outer cases, as described in Chapter 2. The resistivities of these four specimens were measured at ~ 290°K, 273°K, ~ 194°K, ~ 87°K, ~ 77°K, ~ 20°K and then at ~ 5°K prior to storage in liquid helium. Pu. 4 was a specimen of δ phase plutonium stabilised by the addition of 4 At.% Aluminium and its behaviour during self irradiation at low temperatures will be described in the next chapter, it being sufficient to say at this stage that the results obtained from δ Pu. 4 were very significantly different from those obtained from the specimens of plutonium.

The resistivities of the three α phase samples confirmed the results of the first run, rising initially at .091, .093 and .090 $\mu\Omega$ cm/hr.

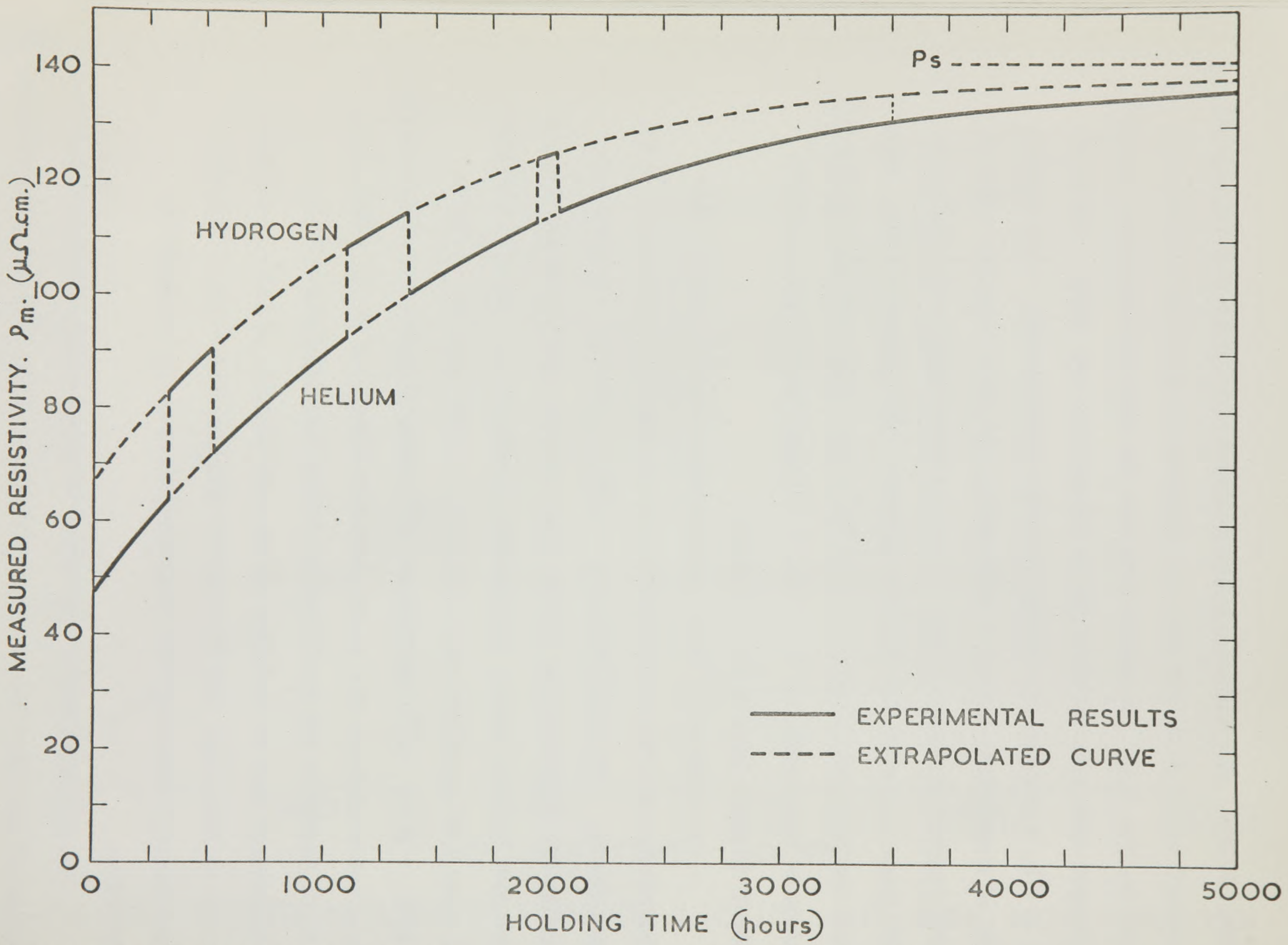


FIG.3.2. MEASURED RESISTIVITY OF Pu 2 AS A FUNCTION OF TIME HELD IN LIQUID HELIUM AND HYDROGEN

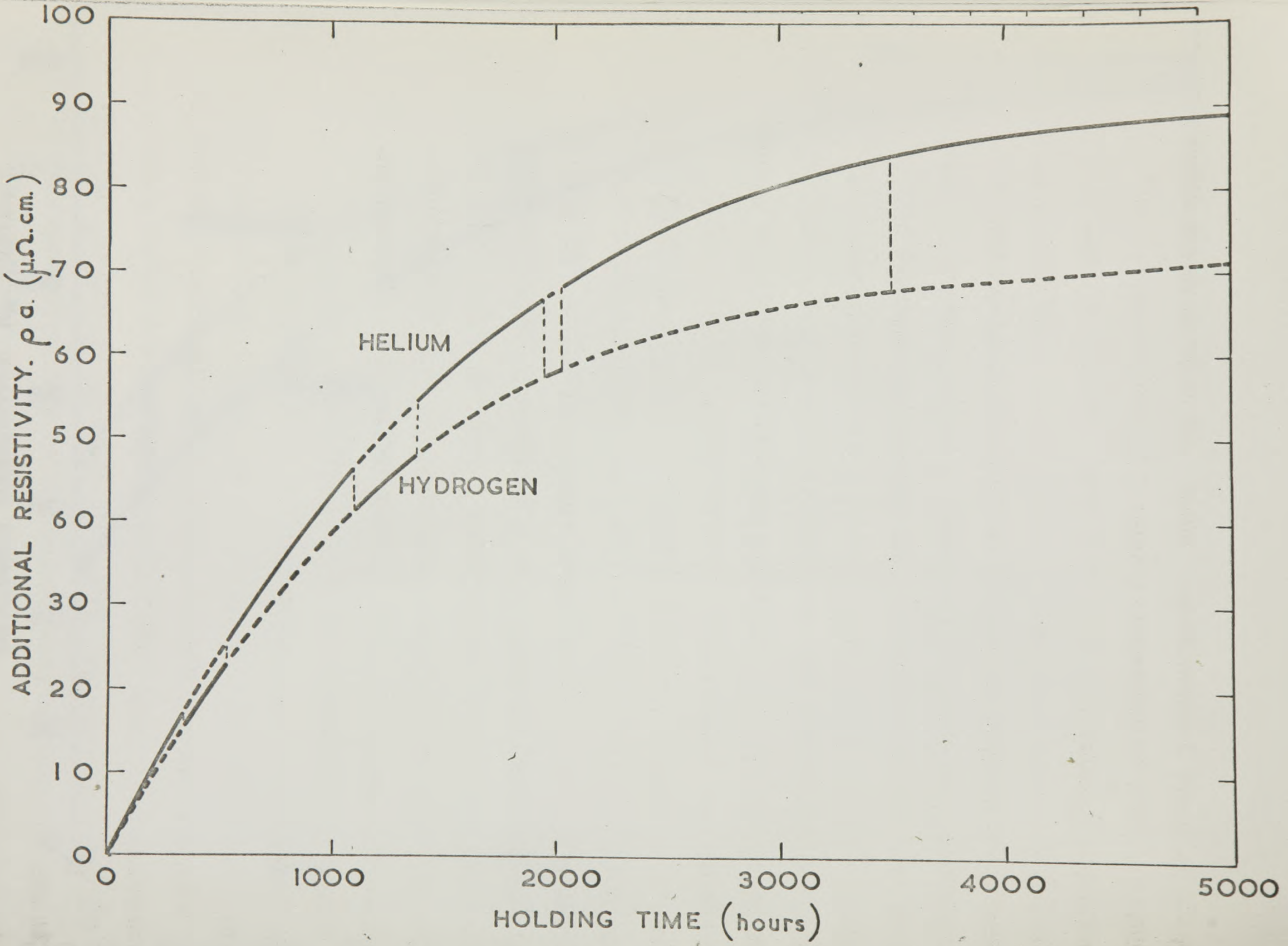


FIG.3.3. ADDITIONAL RESISTIVITY OF Pu2 AS A FUNCTION OF TIME HELD IN LIQUID HELIUM AND HYDROGEN

for Puα 1, 2, and 3 respectively. After ~ 330 hours in liquid helium sample Pu. 2 was transferred to a dewar of liquid hydrogen and its resistivity measured as a function of time. The rate of resistivity rise was then found to be 0.040 $\mu\Omega$ cm/hr. After ~ 140 hours in liquid hydrogen the specimen was returned to liquid helium and its rate of resistivity increase found to be 0.044 $\mu\Omega$ cm/hr., which is the rate which would have been expected if the specimen had never left liquid helium. Thus as well as showing that the rate of resistivity rise decreased with holding time our results also showed conclusively that the rate of resistivity increase was less when the specimen was held in liquid hydrogen than when held in liquid helium. In view of this discrepancy between our results and those of Olsen, et al., sample α Pu.2 was kept at or below ~ 20°K for almost 5,000 hours and periodically transferred between baths of liquid hydrogen and helium. The results of this experiment are shown in Figs. 3.2 and 3.3. Fig. 3.2. shows the measured resistivity as a function of time held below ~ 20°K, while Fig. 3.3. shows the additional resistivity, the measured resistivity - the original resistivity, as a factor of holding time. The essential features of these results may be summarised thus:

a) After warming the specimen from ~ 5°K to ~ 20°K, holding for a short time and then recooling to ~ 5°K, the resistivity measured at ~ 5°K was the same as that which would have been measured if the specimen had remained at ~ 5°K. Similarly after holding for a further period at ~ 5°K and then warming to ~ 20°K, the resistivity measured at ~ 20°K was the same as would have been obtained had the specimen remained at ~ 20°K. Thus none of the damage stored at ~ 5°K was annealed by raising the

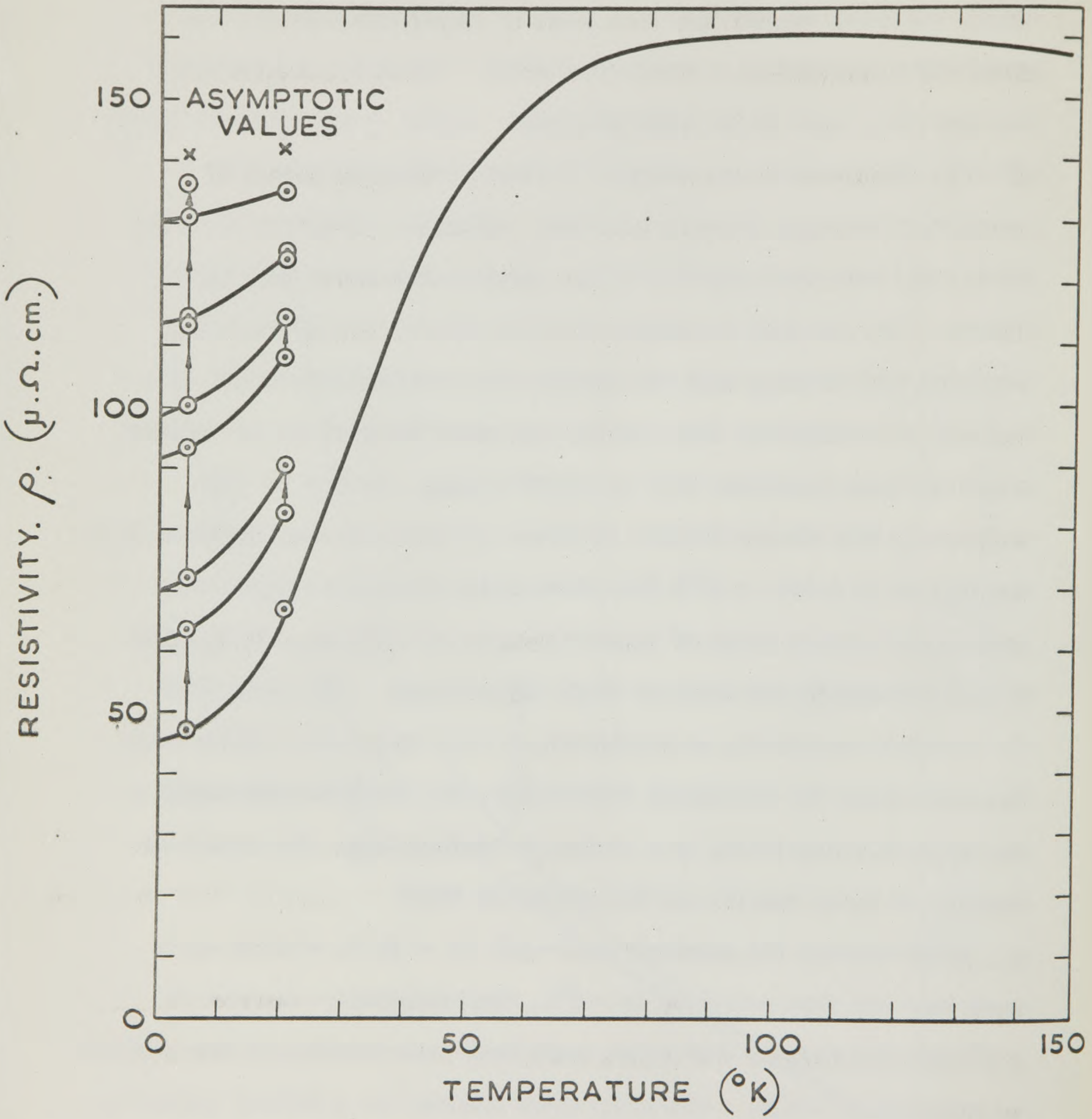


FIG.3.4 RESISTIVITY vs TEMPERATURE CURVES FOR Pu2 IN THE UNDAMAGED AND DAMAGED STATES DURING HOLDING IN LIQUID HELIUM AND HYDROGEN.

temperature to ~ 20°K.

b) The rate of resistivity rise at both temperatures decreased with time, the resistivities approaching almost the same saturation value ρ_s of about 4 $\mu\Omega$cm. as shown in Fig. 3.2.

c) The additional resistivity, ρ_a, due to the same amount of accumulated damage was smaller at ~ 20°K than at ~5°K, as is best seen in Fig. 2.3. in a plot of ρ_a against time. This means that the additional resistivity does not obey Matthiessen's rule, and that the scattering cross section of the defects caused by this radiation damage appears to be temperature dependent. A further way of presenting the data from this experiment is shown in Fig. 3.4. in which the resistivity measured in the undamaged and damaged states is shown as a function of the temperature. It can be seen that as the specimen becomes progressively more damaged the resistivity becomes less temperature dependent, eventually becoming virtually independent of the temperature.

One criticism which may justifiably be levelled at the results shown in Fig. 3.4. is that at only ~ 5°K and ~ 20°K are the resistivities measured, the rest of the curves being a freehand extrapolation of the form suggested by the measured results. In order to overcome this objection and to obviate the necessity of physically transferring specimens from one dewar to another, a process which always involved a small resistance decrease due to slight annealing, a further series of experiments was performed.

Two specimens were cooled by immersion in liquid helium and their resistivities measured at ~ 5°K. They were then raised to progressively higher positions in the neck of the helium dewar and their resistivities

measured at a series of steady temperatures obtained as described in Fig. 2.15, Chapter 2. Thus the resistivity - temperature curves for the unlamaged specimens were obtained. The specimens were then returned to liquid helium and left for a few hundred hours to accumulate self damage. They were then again raised into the neck of the dewar, the resistivities measured as a function of temperature up to 35°K, and the specimens returned once more to liquid helium. The maximum temperature of 35°K was chosen because it was known that the self damage began to anneal at temperatures greater than 40°K. On recooling to liquid helium the resistivities were again measured at ~ 5°K to confirm that no annealing had taken place during warming to ~35°K. The specimens were then left for further periods of time to accumulate self damage, the warming curves being determined at convenient intervals.

We stated at the beginning of this chapter that the work of Olsen et al. showed a slightly greater rate of resistance increase at ~ 20°K than at ~5°K, a result which was contradicted by our work on α Pu. 2. The only possible cause for this discrepancy was considered to be the difference in purity of the plutonium used, the American workers having had access to higher purity material than that used by us. When some higher purity α plutonium became available for experimental purposes we decided to try to resolve this discrepancy. The experiment described above was therefore carried out on two specimens, one of medium purity plutonium, residual resistivity ~ 49 $\mu\Omega$cm. and the other of high purity plutonium, residual resistivity ~ 29 $\mu\Omega$cm. (The plutonium used by the Americans must have been of an even higher purity as its resistivity was about 20 $\mu\Omega$cm.)

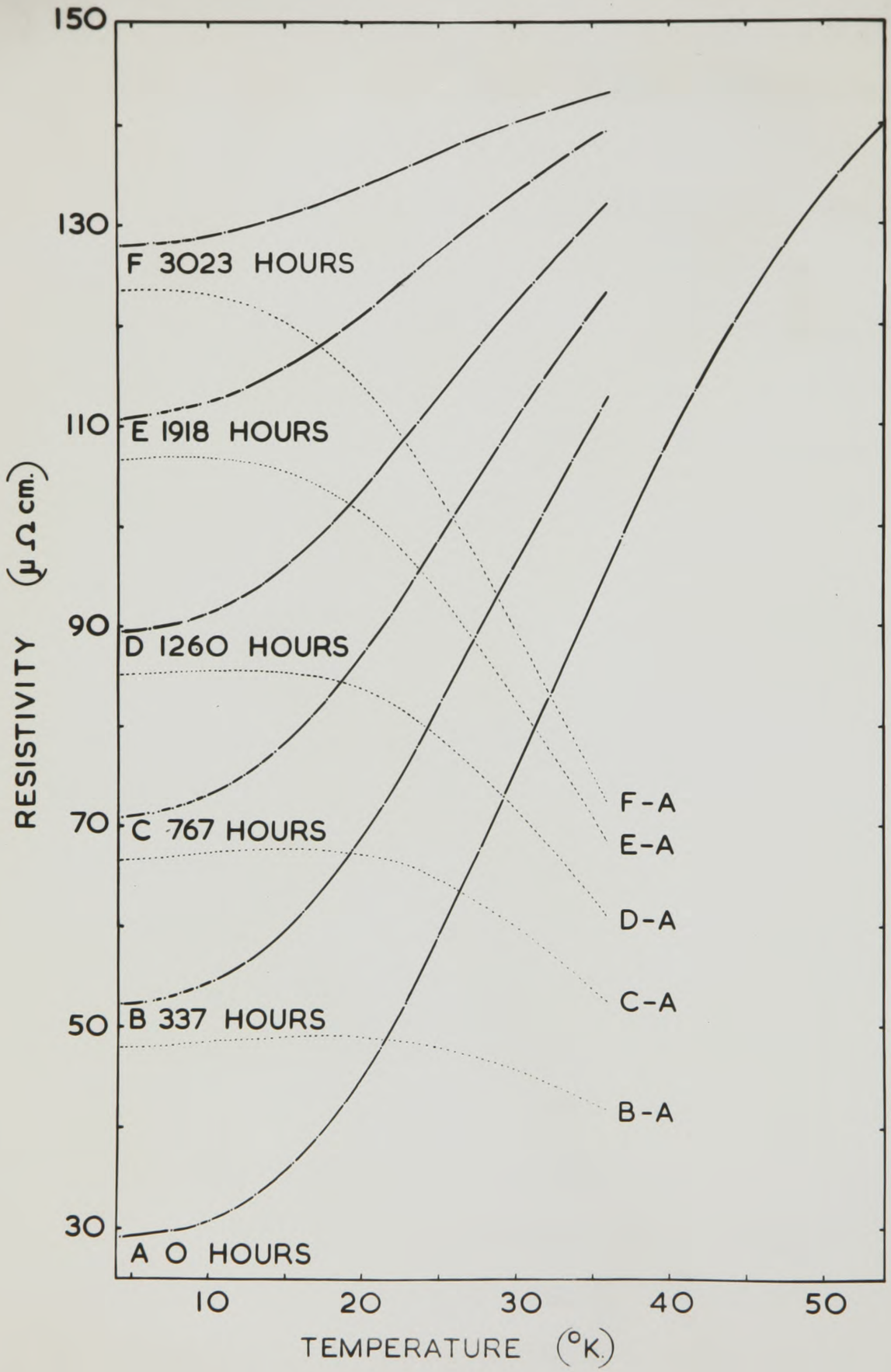


FIG.3.5. Pu8 RESISTIVITY vs TEMPERATURE.

The difference curves B-A etc. are plotted with their zero value coincident with the 25 μΩcm. ordinate.

The results of these experiments are shown in Fig. 3.5. for the high purity Pu. 8 and Fig. 3.6. for the medium purity Pu. 9. In both figures the experimental points are shown on the resistivity-temperature curves and the dashed curves represent the differences between the damaged and the undamaged curves plotted as a function of temperature. Thus if the values of curve A are subtracted from those of curves B, C, D, etc. for corresponding temperatures, the curves B-A, C-A, D-A etc. are obtained. They show the way in which the additional resistivity caused by self-irradiation damage varies with temperature and are not complicated by annealing effects as these are not present below 35°K. Although only two curves were obtained for the medium purity Pu. 9 in the damaged state, (the insulation failed shortly afterwards) the difference between the $\Delta\rho$ vs. T curves of Pu. 9 and those for the high purity Pu. 8 is clearly shown. For the medium purity Pu. 9 $\Delta\rho(20^{\circ}K)$ is always less than $\Delta\rho(5^{\circ}K)$ whereas for the high purity Pu. 8 $\Delta\rho(20^{\circ}K)$ is greater than $\Delta\rho(5^{\circ}K)$ for small values of $\Delta\rho$. Thus for a given small amount of self damage in high purity plutonium there is a slightly greater additional resistivity at $\sim 20^{\circ}K$ than at $\sim 5^{\circ}K$ and thus a slightly higher rate of resistivity increase measured at $\sim 20^{\circ}K$ than at $\sim 5^{\circ}K$. The medium purity material, however, always has $\Delta\rho(5^{\circ}K)$ larger than $\Delta\rho(20^{\circ}K)$ and consequently always has a smaller rate of resistance increase at $\sim 20^{\circ}K$ than at $\sim 5^{\circ}K$.

Finally to recheck the relative rates of damage of high and medium purity plutonium when held at ~ 5 and $\sim 20^{\circ}K$, a sample of high purity plutonium, Pu. 11 and a sample of medium purity Pu. 10, were held in liquid helium and their resistivities measured as a function of time. They were then annealed at room temperature for about a week before

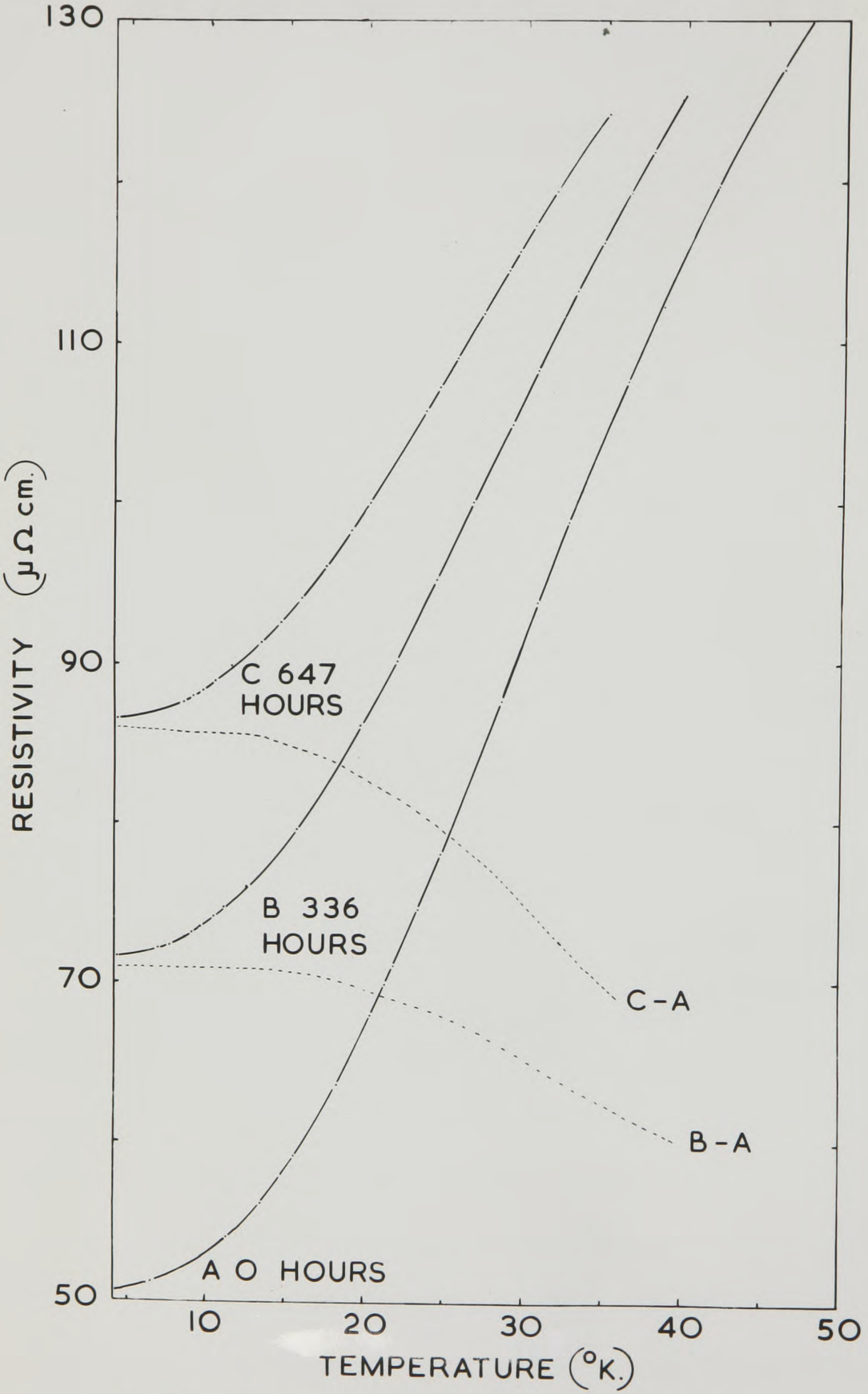


FIG.3.6. Pu9 RESISTIVITY vs TEMPERATURE.

The difference curves B-A etc. are plotted with their zero value coincident with the 50 μΩ cm. ord[illegible]

recooling to liquid hydrogen where their resistivities were measured as a function of time. The results are shown in Table 3.A.

TABLE 3.A.

	Resistivity at start of hold ($\mu\Omega$ cm.)	Average rate of resistivity rise in first 100 hours ($\mu\Omega$ cm/hr)
Pu. 10 @ 5°K	52.27	0.072_2
Pu. 10 @ 20°K	70.41	0.061_8
Pu. 11 @ 5°K	22.79	0.067_3
Pu. 11 @ 20°K	43.28	0.068_8

It can be seen from these figures that the rate of resistivity increase for the pure plutonium was slightly greater at $\sim 20^{\circ}K$ than at $\sim 5^{\circ}K$. The difference was, however, slightly less than that found by Olsen and Elliott.

3.2. Analyses of the Resistivity vs. Temperature curves of alpha plutonium in the Undamaged and Damaged states

In his thesis Meaden stated that analyses of his results showed that the "ideal" resistance of α plutonium obeyed a $\rho_i \propto T^n$ law below $\sim 30^{\circ}K$, where n was between 2.0 and 2.4 depending on the purity of the specimen. (The "ideal" resistance is obtained by subtracting the residual resistance from the measured resistance at any temperature. The inverted commas are included because, for plutonium, the resistance thus obtained has a far from ideal temperature dependence.) The results of Olsen and Elliott (1962) were stated not to show this $\rho_i \propto T^n$

behaviour but to show that the measured resistivity obeyed a power law of the type $\rho_m \propto T^n$ between ~20 and ~47°K, where n was approximately unity. Furthermore Smoluchowski (1962) stated that his analysis of low temperature resistivity vs. temperature data, taken from an unnamed, presumably American, source, showed that below ~ 30°K $\rho_i \propto e^{-1/T}$; i.e. the ideal resistivity had an exponential temperature dependence. In order to try to shed some light on this matter we decided to analyse the low temperature resistivity vs. temperature data taken from α Pu. 8 and α Pu. 9 both for the undamaged and damaged states.

Before presenting our analyses we would like to stress certain points. Any analysis of low temperature resistance data which computes the ideal resistance will be heavily dependent on the value assumed for the residual resistance. In the case of Meaden's data his lowest point was taken at 1.54°K by which stage the resistance was virtually temperature independent. Calculation of the residual resistance involved, therefore, only a small extrapolation to zero temperature. In our case the lowest data point was taken at 4.2°K and an extrapolation of the order of 0.5 $\mu\Omega$ cm. was necessary to obtain the residual resistivity. Furthermore in Meaden's experiments his specimens were in intimate contact with liquid helium for all readings taken at or below 4.2°K. In contrast our use of canned specimens meant that the self- and Joule heat had to be dissipated to the coolant via an exchange gas. It was therefore much more likely that temperature gradients existed along our specimens than along those used by Meaden. Finally, in contrast to Meaden's use of a carbon resistance thermometer below ~ 20°K, our use of Gold - 2.1 At.% Cobalt vs. Copper thermocouples gave considerably less accurate temperatures in the range ~ 20 to ~ 5°K. The necessity of plotting results on logarithmic and

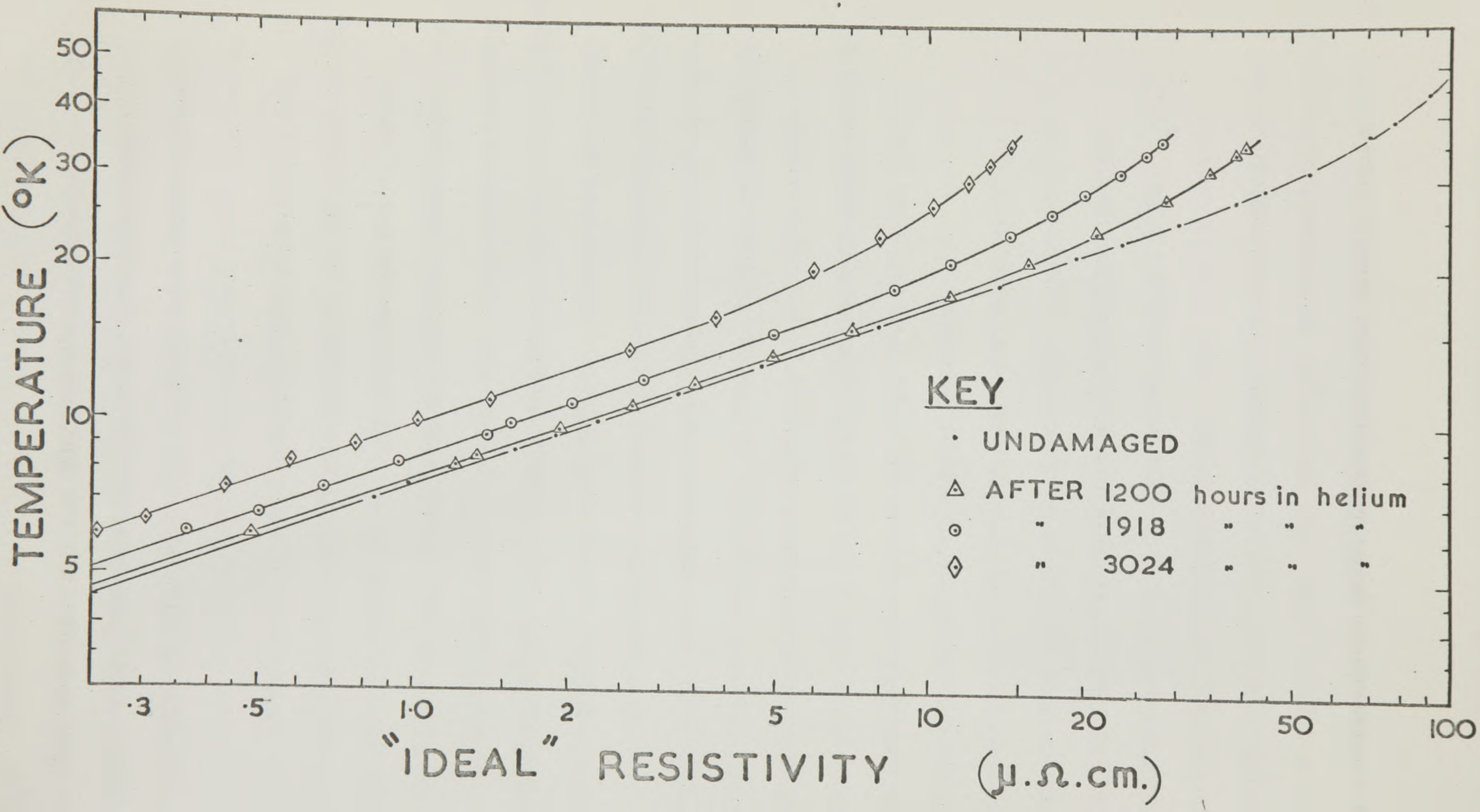


FIG. 3.7. Pu.8. LOGARITHMIC ANALYSIS OF RESISTIVITY vs TEMPERATURE IN UNDAMAGED AND DAMAGED STATES.

$^1/T$ scales put unfortunately large emphasis on these less reliable low temperature results. With these limitations in mind we have not plotted any of our data points taken below $6^\circ K$ in the analyses which will now be presented in Figs. 3.7 to 3.13.

In Fig. 3.7. we show log ρ_i plotted against log T for the high purity α Pu. 8. It can immediately be seen that, not only for the undamaged state but also for the damaged states, a plot of log ρ_i vs. log T yields a linear relationship. Thus not only is $\rho_i \propto T^n$ at very low temperatures but, as all the lines in Fig. 3.7. are parallel, the index n of this power law is constant and not affected by the self-irradiation damage. From the slopes of the lines in Fig. 3.7., $n = 2.8_0$. Further inspection of the results shown in Fig. 3.7. and on a larger scale in Fig. 3.8. will indicate that for the undamaged specimen the power law is obeyed up to $\sim 20^\circ K$, above which temperature the resistivity increases at a greater rate than that given by the law. As the specimen becomes progressively more damaged, the maximum temperature at which the law is obeyed decreases, reaching $\sim 14^\circ K$ after ~ 3024 hours in liquid helium.

Having found that the law $\rho_i = K T^n$ is obeyed for the resistivity vs. temperature data both in the undamaged and damaged states, the proportionality coefficients K can be found by substituting the actual values of ρ_i and T for any temperature at which the law is valid. Table 3.B. gives these coefficients K and the temperatures below which they are valid.

One point which emerges from this analysis correlates with the point made earlier about pure plutonium having a greater resistivity increase at $\sim 20^\circ K$ than at $\sim 5^\circ K$ for small damage accumulations.

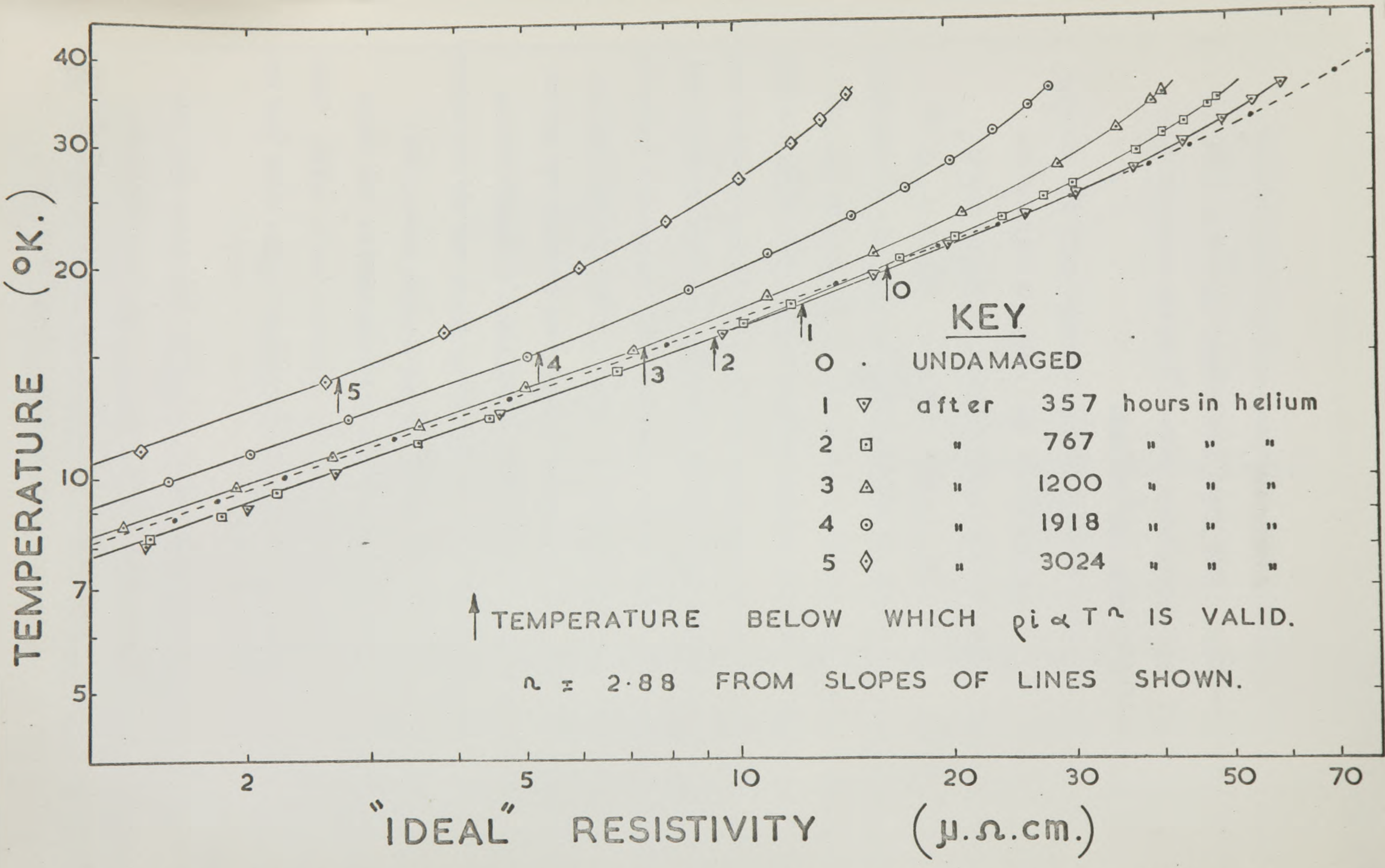


FIG.3.8. Pu.8. LOGARITHMIC ANALYSIS OF RESISTIVITY vs TEMPERATURE DATA.

TABLE 3.B.

Analysis of resistivity vs. temperature data for Pu. 8 as $\rho_i = KT^n$, n = 2.88

State	Holding time in liquid helium (hours)	Maximum temperature at which law is valid (°K)	Proportionality Coefficient ($\mu\Omega$ cm/°K^n)
Undamaged	0	~ 20	2.9_6 x 10^{-3}
1st damaged	357	~ 17.5	3.3_6 "
2nd "	767	~ 16.0	3.3_6 "
3rd "	1200	~ 15.5	2.7_2 "
4th "	1918	~ 15.0	2.1_2 "
5th "	3024	~ 14.0	1.3_7 "

As the coefficient K increases from 2.9_6 to 3.3_6 after ~ 350 hours in helium, the change in resistance $\Delta\rho_{20°K}$ is greater than $\Delta\rho_{5°K}$ as $\Delta\rho_{20°K} - \Delta\rho_{5°K} = (K_1 - K_0)(20^n - 5^n) \simeq +2\ \mu\Omega$ cm. This analysis is valid as the law $\rho_i \propto T^n$ holds to at least 20°K for both curves. Although the $\rho_i \propto T^n$ law does not hold for temperatures greater than approximately 16°K once the specimen has been irradiated for 1200 hours at ~ 5°K, we will calculate $\Delta\rho\ 20°K - \Delta\rho\ 5°K$ on the assumption that the law is valid. Then $\Delta\rho_{20°K} - \Delta\rho_{5°K} = (K_3 - K_0)(20^n - 5^n) \simeq -1.3\ \mu\Omega$ cm. In fact the difference will not be quite so large as this because of the deviation from the law $\rho_i \propto T^n$.

Before proceeding to consider our analyses of resistivity temperature data for temperatures higher than those for which the law $\rho_i = K T^n$ is valid, we will complete our discussion of the very low temperature data by considering the analysis of the results from medium purity Pu. 9. These are shown in Fig. 3.9. in which log ρ_i is

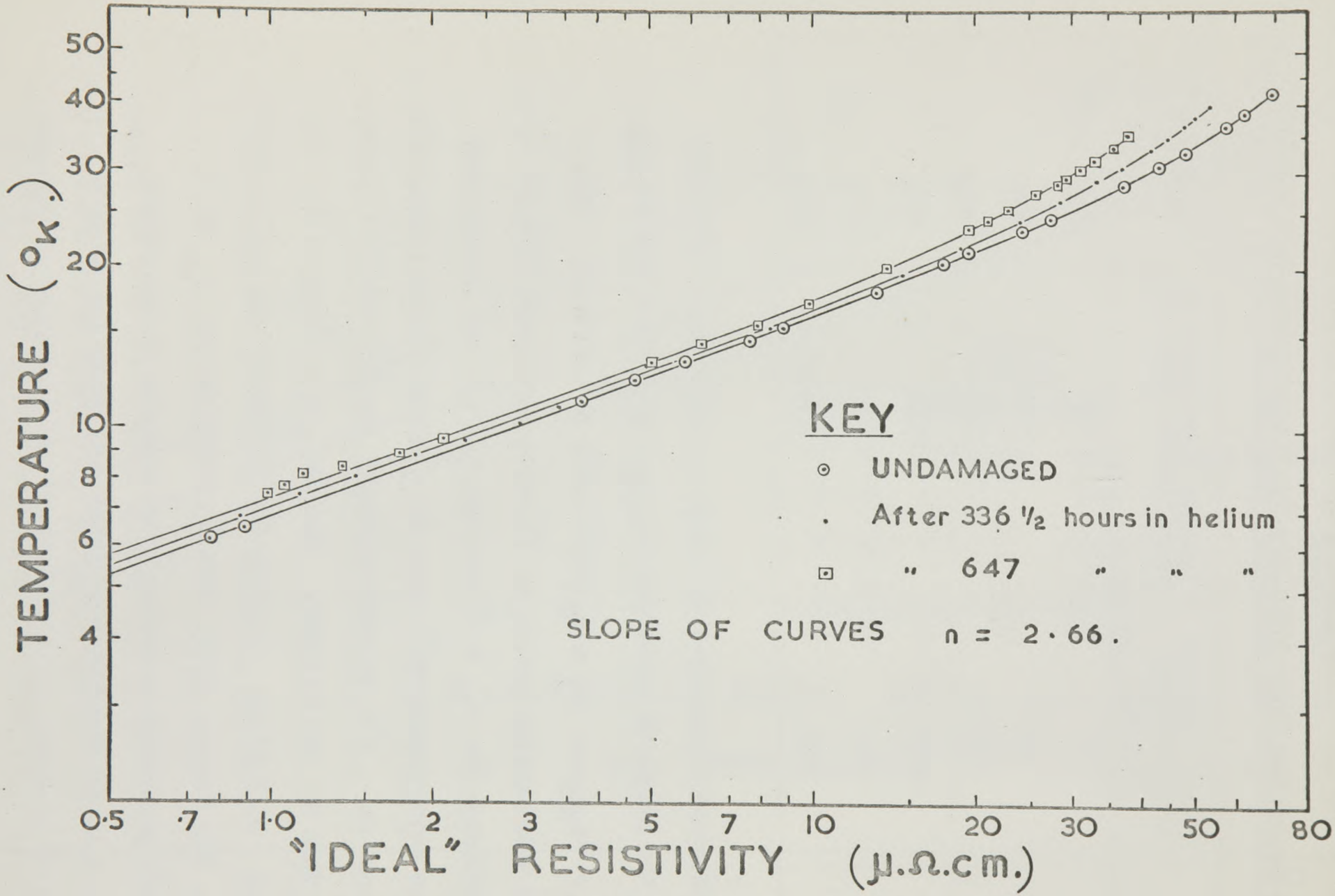


FIG. 3.9. Pu.9. LOGARITHMIC ANALYSIS OF RESISTIVITY vs. TEMPERATURE DATA IN UNDAMAGED AND DAMAGED STATES.

plotted against log T. The linear relationship is not quite so well obeyed as for Pu. 8; nevertheless the results still show the same essential features. The slope of the lines is in this case n = 2.66. The proportionality coefficients and the temperatures below which the law is valid are shown in Table 3.C.

TABLE 3.C.

State	Holding time in liquid helium (hours)	Maximum temperature at which law is valid (°K)	Proportionality Coefficient ($\mu\Omega$ cm/°K^n)
Undamaged	0	~ 17	$5.9_6 \times 10^{-3}$
1st Damaged	336½	~ 16	5.4_6 "
2nd Damaged	647	~ 15	5.0_4 "

It can be seen that both the coefficient K and T max. decrease steadily as the sample becomes more damaged and hence in contrast to the high purity Pu. 8, even for the smallest damage accumulation $\Delta\rho_{20°K} < \Delta\rho_{5°K}$. The significance of the lower index n and the lower temperatures below which the law is valid is not at this stage clear. The data does, however, follow the same pattern as that indicated by Meaden, namely lower indices for the lower purity material.

We will return now to investigate Smoluchowski's claim that below ~ 30°K the ideal resistivity of α and δ plutonium obeys the exponential law $\rho_i \propto e^{-1}/T$. To do this we have analysed our data for samples Pu. 8 and Pu. 9 both in the undamaged and damaged states and also data taken by Meaden and kindly made available to us by him. In every case we have been unable to obtain confirmation of an exponential temperature

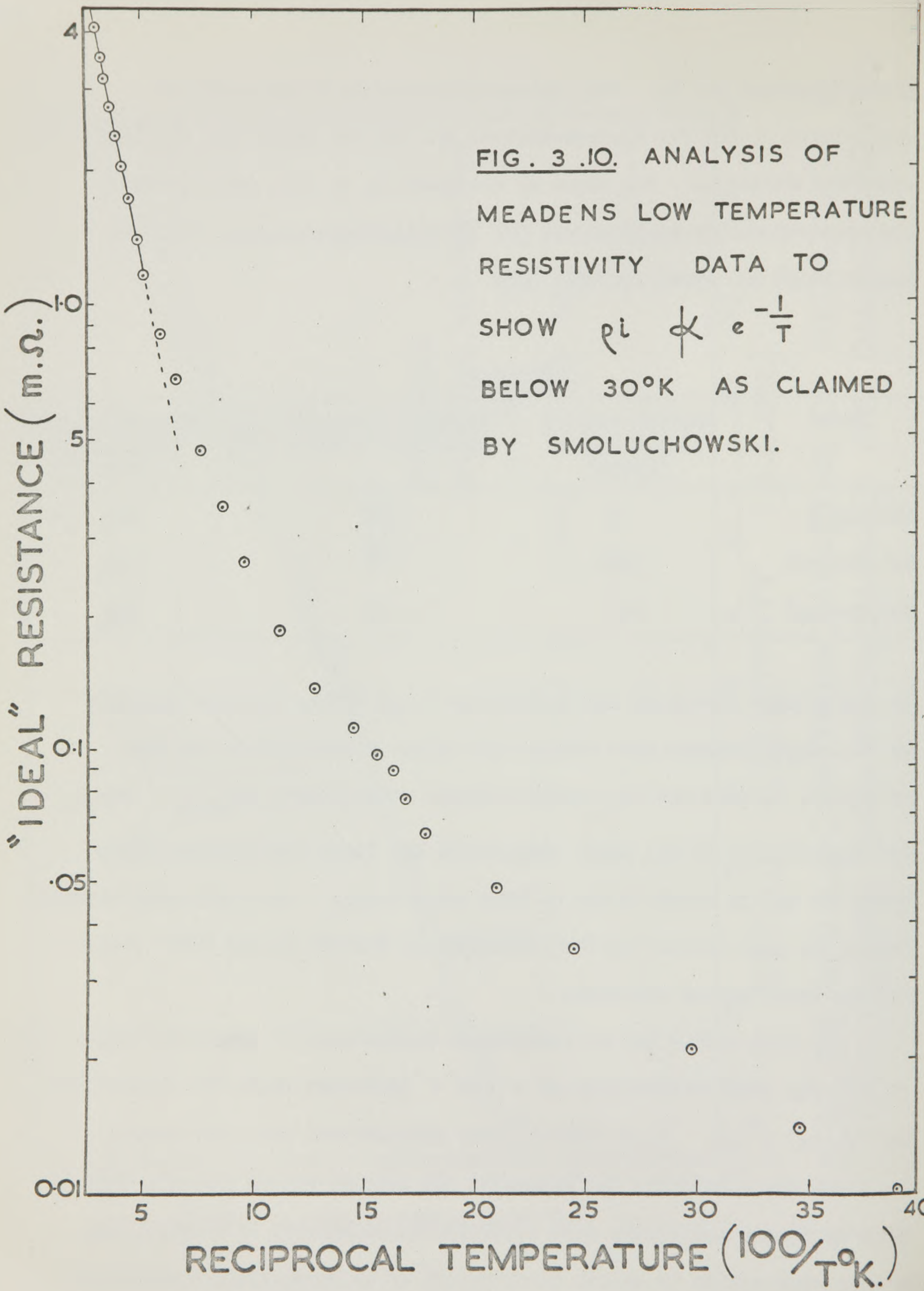
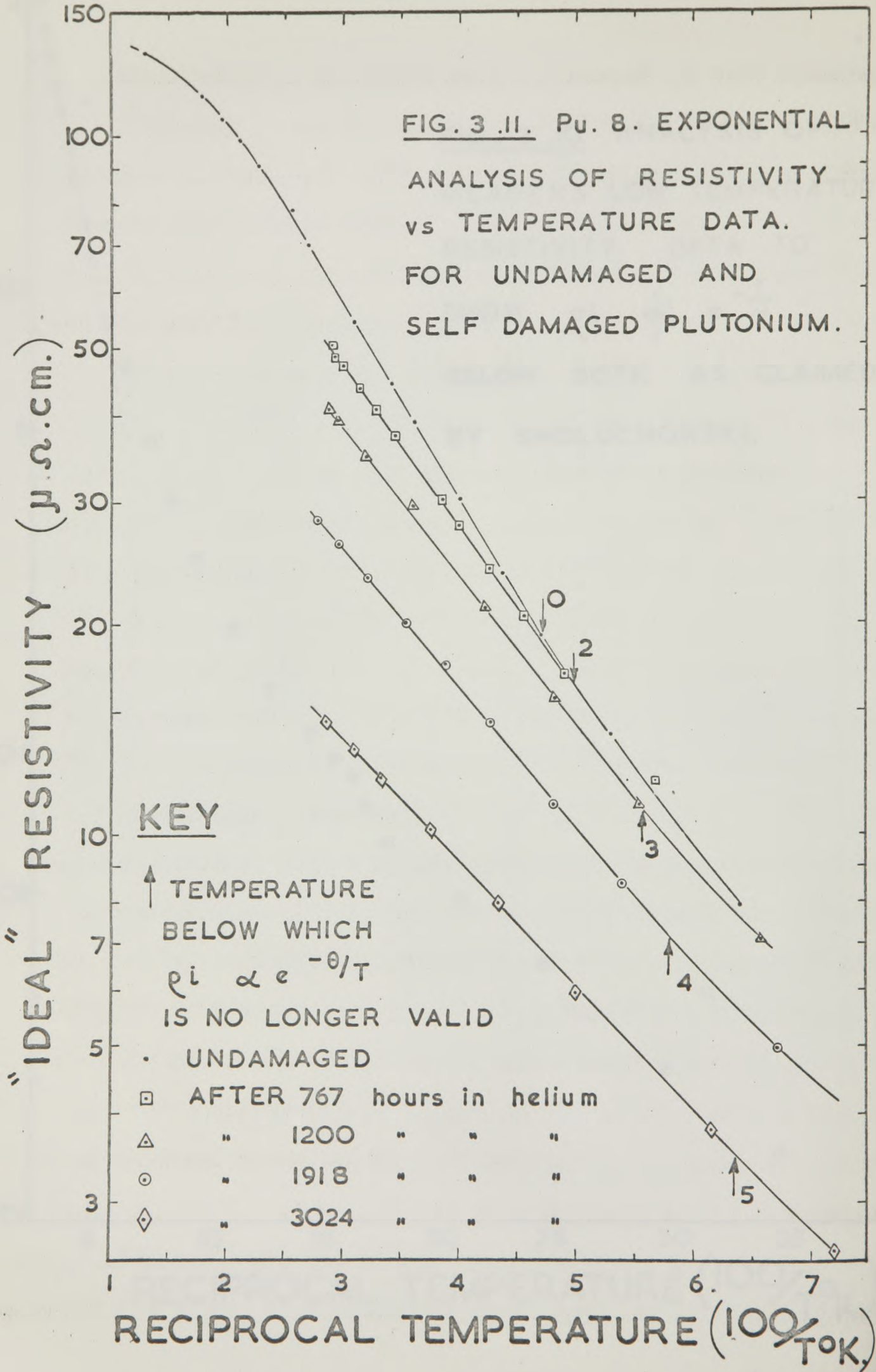


FIG. 3.10. ANALYSIS OF MEADENS LOW TEMPERATURE RESISTIVITY DATA TO SHOW $\rho i \propto e^{-\frac{1}{T}}$ BELOW 30°K AS CLAIMED BY SMOLUCHOWSKI.


FIG. 3 .11. Pu. 8. EXPONENTIAL ANALYSIS OF RESISTIVITY vs TEMPERATURE DATA. FOR UNDAMAGED AND SELF DAMAGED PLUTONIUM.
"IDEAL" RESISTIVITY (μ.Ω.cm.)
150
100
70
50
30
20
10
7
5
3
1
2
3
4
5
6.
7
RECIPROCAL TEMPERATURE (100/T°K)
KEY
TEMPERATURE BELOW WHICH ρi ∝ e^-θ/T IS NO LONGER VALID
UNDAMAGED
AFTER 767 hours in helium
" 1200 " " "
" 1918 " " "
" 3024 " " "
0
2
3
4
5

dependence over the temperature range stipulated by Smoluchowski. In Fig. 3.10. Meaden's results are plotted as log ρ_i against $^1/T$ showing no linear relationship below ~ 25°K. (We have used Meaden's data in preference to our own because his lowest data point taken at 1.34°K required a smaller and more accurate extrapolation to absolute zero than our lowest data point at 4.2°K.) Although no linear relationship between log ρ_i and $^1/T$ was obeyed below ~ 25°K it was found that such a linear relationship existed between ~ 20 and ~ 30°K.

Accordingly we have analysed our data for Pu. 8 and Pu. 9 in the undamaged and damaged states. The results are shown in Fig. 3.11. for the high purity Pu. 8 and in Fig. 3.12. for the medium purity Pu. 9. In all cases a linear relationship exists between log e ρ_i and $^1/T$ over some temperature range. Considering Fig. 3.11., it can be seen that for the undamaged specimens a linear relationship between log e ρ_i and $^{100}/T$ exists between $^{100}/T$ = 2.4 and 4.7$_5$, i.e. between T = ~42°K and ~ 21°K. As the specimen becomes progressively more damaged the temperature below which the relationship is invalid decreases, becoming ~15.8°K after 3024 hours of self-damage. As no measurements were taken in the damaged state at temperatures greater than ~ 35°K to prevent the occurrence of annealing, it is impossible to say whether there was also a self-damage induced change in the maximum temperature at which the relationship $\rho_i \propto e^{-1/T}$ is valid. A further feature which is obvious from Fig. 3.11 is that the slope of the curves decreases as the specimen becomes more damaged.

Now if $\rho_i = A\, e^{-\Theta/T}$, then $\ln \rho i = \ln A - \Theta/T$; thus if $\ln \rho_i$ is plotted against $^1/T$ the characteristic temperature Θ appears as the slope

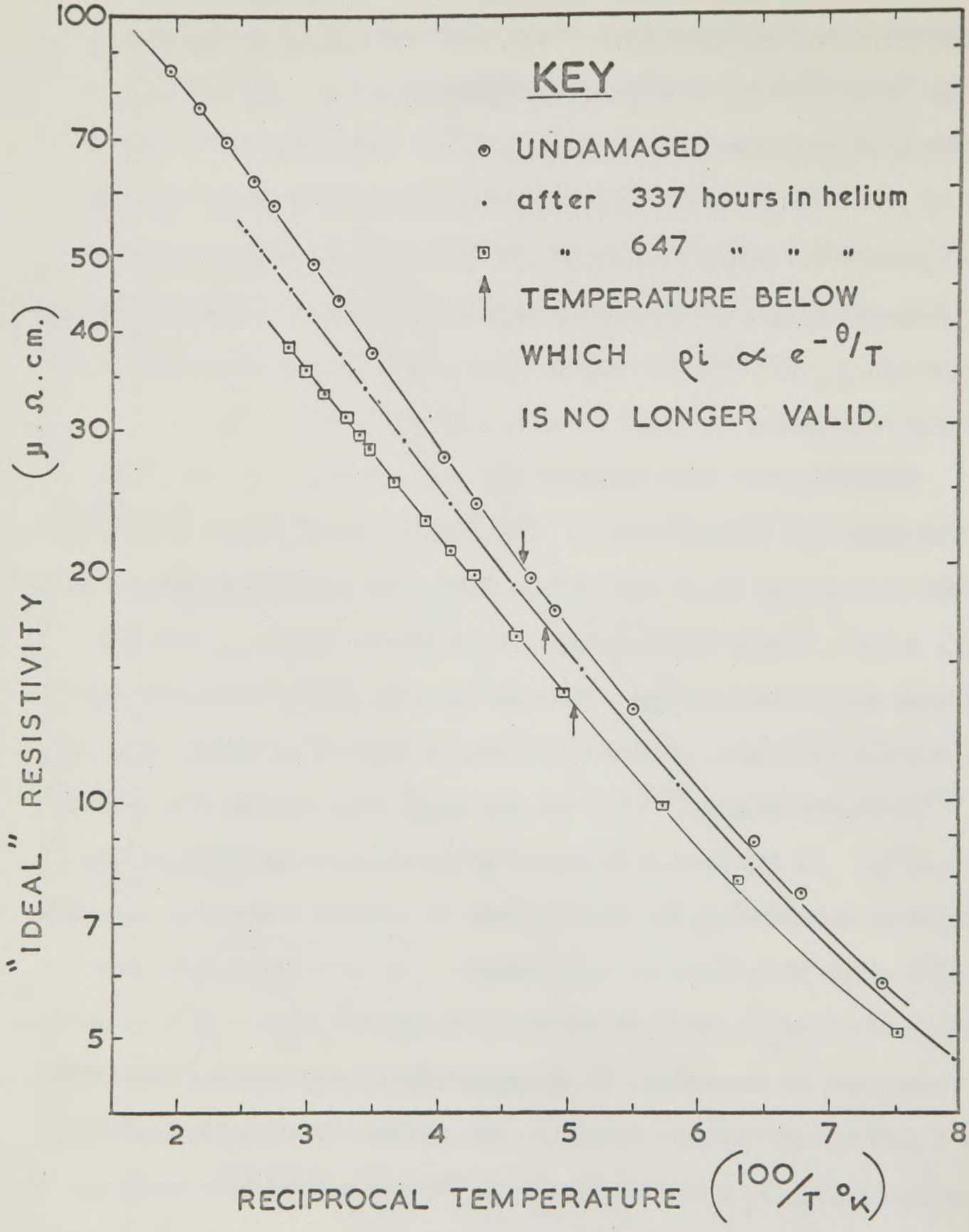


FIG.3.12.Pu. 9. EXPONENTIAL ANALYSIS OF RESISTIVITY vs TEMPERATURE DATA FOR UNDAMAGED AND DAMAGED PLUTONIUM.

of the resultant straight line. (In fact the values of the slopes of Figs. 3.11 and 3.12 have to be multiplied by 2.303 as they were plotted as logs to the base 10 instead of to the base e.) In Table 3.D. we show the characteristic temperature Θ thus obtained, the minimum temperature at which the relationship $\rho_i \propto e^{-\Theta/T}$ is valid, T min., and the proportionality coefficients A, for Pu. 8 in the undamaged and damaged states.

TABLE 3.D.

Analysis of resistivity vs.temperature data for Pu. 8 as $\rho_i = A\, e^{-\Theta/T}$.

State	Time held in helium (hours)	Minimum temperature law valid T min ($^\circ$K)	Characteristic temperature Θ ($^\circ$K)	Proportionality Coefficient A ($\mu\Omega$ cm.)
Undamaged	0	~ 21	64.7	410
1st Damaged	357	~ 20	57.3	299
2nd "	767	~ 20	53.3	234
3rd "	1200	~ 17.9	49.3	169
4th "	1918	~ 17.2	46.1	103
5th "	3024	~ 15.8	40.6	46.5

We have also carried out a similar analysis of the results obtained from the medium purity Pu. 9 in the undamaged and damaged states. They are shown in Fig. 3.12 where log ρ_i is plotted against $^{100}/_T$. Once more the law $\rho_i = A\, e^{-\Theta/T}$ is found to be valid and the corresponding values of the coefficients Θ, T min. and A are shown in Table 3.E. As might have been expected the values of A and Θ for the medium purity sample in the undamaged state are less than those for the high purity sample in the undamaged state.

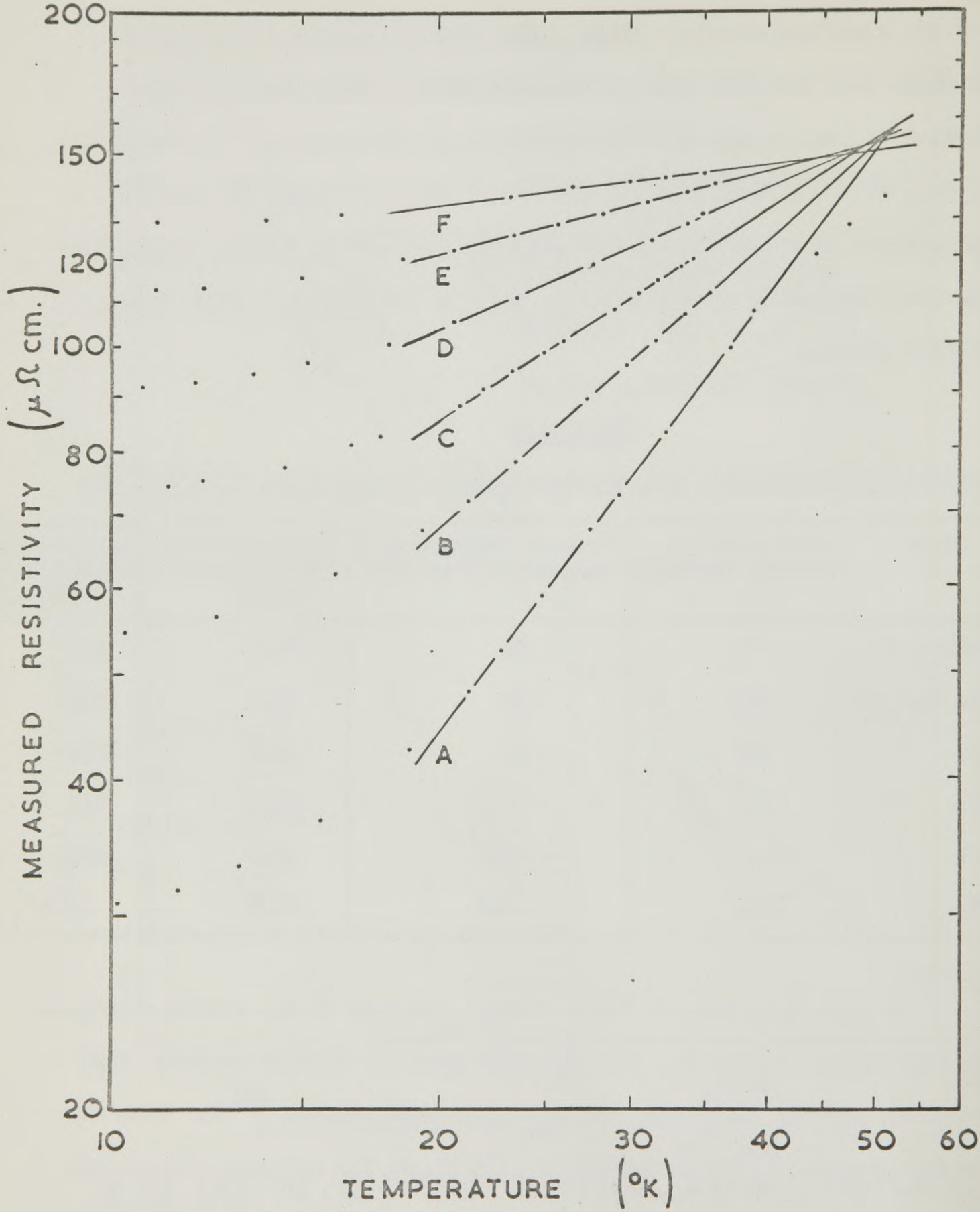


FIG. 3.13. Pu8. LOGARITHMIC ANALYSIS OF MEASURED RESISTIVITY vs TEMPERATURE IN UNDAMAGED AND DAMAGED STATES.

TABLE 3.E.

Analysis of resistivity vs. temperature data for Pu. 9 as $\rho_i = A e^{-\theta/T}$

State	Time held in helium (hours)	Minimum temperature law valid T min.(°K)	Characteristic temperature θ (°K)	Proportionality Coefficient A ($\mu\Omega$ cm.)
Undamaged	0	~ 22.5	54.7	251.5
1st Damaged	337	~ 21.5	50.8	192.5
2nd Damaged	647	~ 20.5	48.0	149.2

We have indicated in an earlier chapter that the validity of the separation of the electrical resistance of plutonium into "ideal" and residual components is highly questionable, especially if α plutonium were proved to be antiferromagnetic. Furthermore Olsen & Elliott (1962) reported that they found that between ~ 19°K and ~ 47°K their low temperature resistivity data obeyed the power law $\rho_m = B T^n$, where ρ_m was the measured resistivity. The index n was found to be approximately unity and to be somewhat higher for their higher purity than for their lower purity samples. We have therefore analysed our results for Pu. 8 in the above manner and in Fig. 3.13, log ρ_m is shown as a function of log T for the undamaged and damaged states. The letters A to F which label the curves, correspond to those of Fig. 3.5. It can be seen that there is a linear relationship between log ρ_m and log T between ~ 20°K and ~ 40°K for all of the plots. It would also appear that most of the straight lines meet at approximately 50°K at a value of ~ 150 $\mu\Omega$ cm. and that the index n decreases steadily as the specimen becomes more damaged. The values of n for the different degrees of self damage are shown in Table 3.F. together with the appropriate residual resistivities.

TABLE 3.F.

State	Hours at ~ 5°K	Index n	Residual Resistivity ($\mu\Omega$ cm.)
Undamaged	0	1.33	28.6_0
1st Damaged	357	1.11	31.9_0
2nd Damaged	767	0.52	70.9_4
3rd Damaged	1200	0.42	89.2_8
4th Damaged	1918	0.25	110.9_0
5th Damaged	3024	0.12	127.9_8

A similar analysis has been performed on the results obtained from α Pu. 9. The linear relationship is not quite so well defined as for α Pu. 8 and exists between ~ 22°K and ~ 38°K. The coefficients, n, are, as expected, lower than for the purer Pu. 8 and are shown in Table 3.G.

TABLE 3.G.

State	Hours at ~ 5°K	Index n	Residual Resistivity ($\mu\Omega$ cm.)
Undamaged	0	0.83	50.38
1st Damaged	336½	0.57	71.22
2nd Damaged	647	0.40	86.26

The straight lines defined by the relationship log $\rho_m \propto$ log T also appear to meet at approximately 50°K but at a lower resistivity of ~ 145 $\mu\Omega$cm.

To summarise this section on the analysis of the low temperature resistivity vs. temperature data of undamaged and self damaged plutonium we would make the following points:

1) At the lowest temperatures, analysis of our data shows that the "ideal" resistivity obeys the power law $\rho_i = K T^n$ and that although the coefficient K decreases as the specimen becomes more damaged, the index n remains unchanged. Our values of $n = 2.8_9$ and 2.6_6 for high and medium purity plutonium respectively are higher than those of 2.4 and 2.0 found by Meaden. The significance of this is not apparent.

2) At temperatures a few degrees higher than those for which the power law is valid an exponential behaviour of the form $\rho_i = A e^{-\theta/T}$ can be found. As the specimens become more damaged the values of θ and A both decrease steadily.

3) At temperatures greater than $\sim 45^{\circ}K$ the resistivity increases less rapidly than exponentially for the undamaged specimen. The maximum temperature at which the relationship is valid for the damaged specimen is unknown because annealing of the self damage sets in at about $40^{\circ}K$.

4) The exponential behaviour $\rho_i = A e^{-\theta/T}$ is not valid from $\sim 30^{\circ}K$ down to absolute zero as required by Sadluchowski. In order to force such a fit unjustifiably large errors in either the resistivity or temperature must be assumed.

5) An alternative analysis of the measured resistivity as a function of temperature shows that $\rho_m \propto T^n$ between $\sim 20^{\circ}K$ and $\sim 40^{\circ}K$ and that the index n decreases as the specimen becomes more damaged.

6) Even a cursory examination of Figs. 3.5. and 3.6. shows that the measured resistivity is approximately proportional to the temperature over some temperature range, usually between ~ 20 and $\sim 40^{\circ}K$ as there is a point of inflexion in each of the curves in this temperature range.

In view of the many ways in which our data can be analysed we

would hesitate before indicating a preference for any one analysis. Furthermore until there are satisfactory reasons for choosing one analysis in preference to the others we do not feel justified in following the suggestion made by Lee (priv. comm.) that the curve for completely pure α plutonium might be obtained by extrapolating the analysis of our data back to zero residual resistivity. In case any future theoretical development of the theory of the low temperature behaviour of plutonium should call for further analysis of our results, we have included in Appendix II our measured values of the resistivity as a function of temperature for Pu. 8 and Pu. 9 in the undamaged and damaged states.

3.3. An Analysis of the Rates of Resistivity increase in alpha plutonium as a function of the time held in liquid helium

We will now return to consider the results of the 5,000 hour liquid helium run on Pu.2, shown in Fig. 3.3., where the additional resistivity produced by self damage is plotted as a function of holding time. From the shape of these curves it seemed possible that the additional resistivity ρ_a was following an exponential build in of the form

$$\rho_a = (\rho_\infty - \rho_o)(1 - e^{-\alpha t}) \qquad \text{3.i.}$$

Analysis of the readings taken from Pu.2 while held in liquid helium showed that although this was approximately true, the relationship did not hold perfectly. It was possible that this failure was due to the slight annealing which accompanied the transfer of the specimen from one storage dewar to another.

In order to remove this objection two specimens, α Pu.5 and α Pu.6, were held in liquid helium for up to 8,000 hours and at no time during

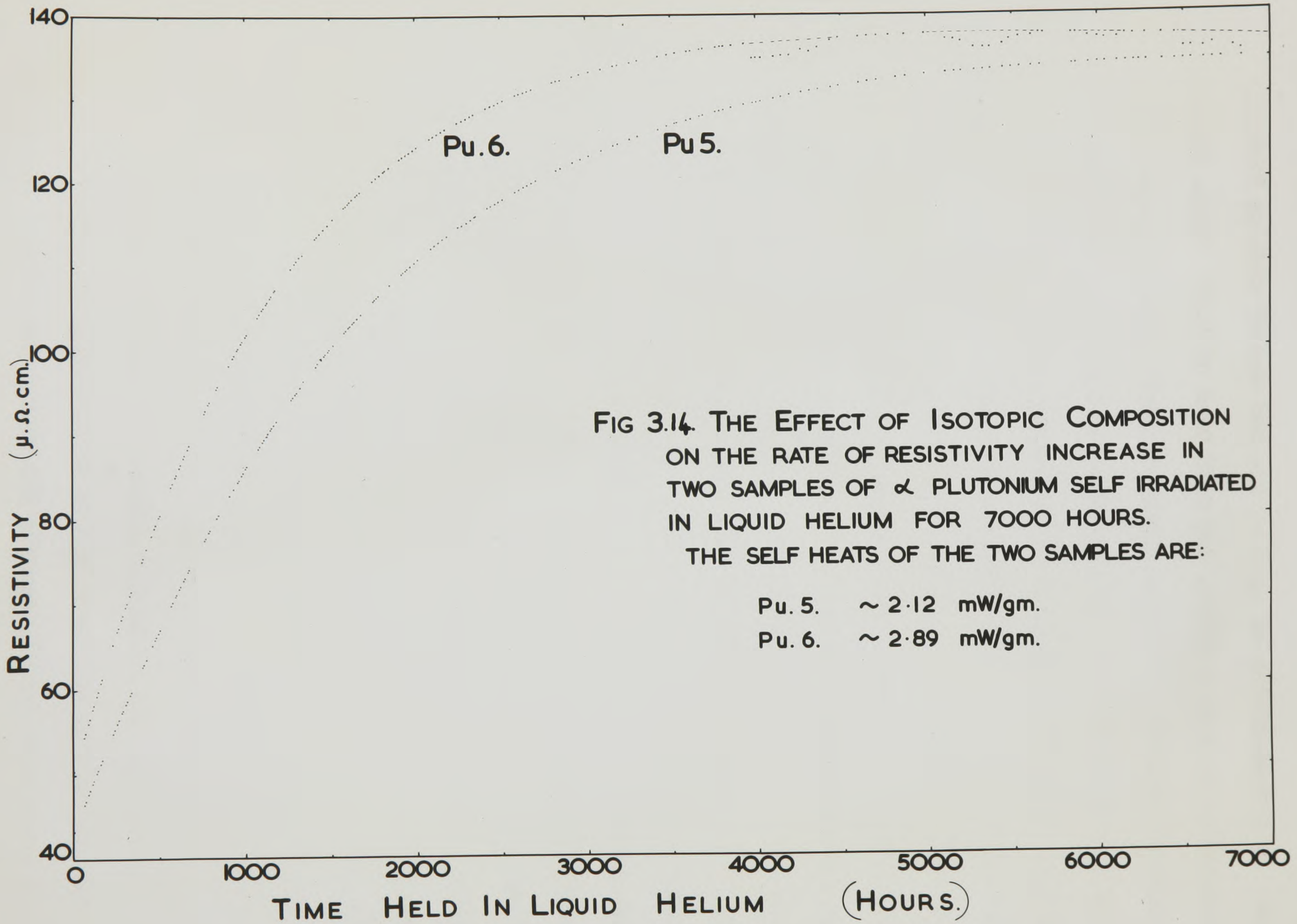


FIG 3.14. THE EFFECT OF ISOTOPIC COMPOSITION ON THE RATE OF RESISTIVITY INCREASE IN TWO SAMPLES OF α PLUTONIUM SELF IRRADIATED IN LIQUID HELIUM FOR 7000 HOURS.
THE SELF HEATS OF THE TWO SAMPLES ARE:

Pu. 5. ~ 2·12 mW/gm.
Pu. 6. ~ 2·89 mW/gm.

this period did the temperature rise to more than ~ 5°K. Pu. 5 had an initial ~ 5°K resistivity of 43.2 μΩ cm. and was of such an isotopic composition as to have a calculated self heat of 2.124 mW/gm. whereas Pu. 6 had an initial ~ 5°K resistivity of 49.9 μΩ cm. and a calculated self heat of 2.894 mW/gm. It was thus possible to compare the self damage behaviour of two samples of different purities and isotopic compositions. The results of this experiment are shown in Fig. 3.14. in which the measured resistivity is plotted as a function of time held in liquid helium. The results are presented in photographic form because it was found impossible to obtain sufficient detail by ordinary dia-line or similar reproductive techniques. Even so the estimated experimental error of each reading is less than the diameter of the dot used to represent that reading. Examination of Fig. 3.14. will show that the standard deviation from a smooth curve is also of this magnitude. It will also be seen that after almost 4,000 hours in liquid helium, the resistivity of Pu.6 decreased suddenly by almost 2 μΩ cm. but that it apparently returned to the original curve after ~ 4,500 hours. Similar deviations occurred between ~ 5,000 and 5,700 hours at ~ 5,900 and 6,100 hours while after ~ 6,400 hours the readings became rather erratic and unreliable. This was probably caused by a loose potential contact on the specimen, or possibly by an intermittent partial short between the potential wires in the lead harness. This undoubtedly reduces the value of the results, but the essential patterns are nevertheless discernible. Pu. 6 with its higher self heat builds in initially at a greater rate than Pu. 5 and tends more quickly towards its asymptotic value. Due to the unreliability of the results on Pu. 6 after 4,000 hours the actual value

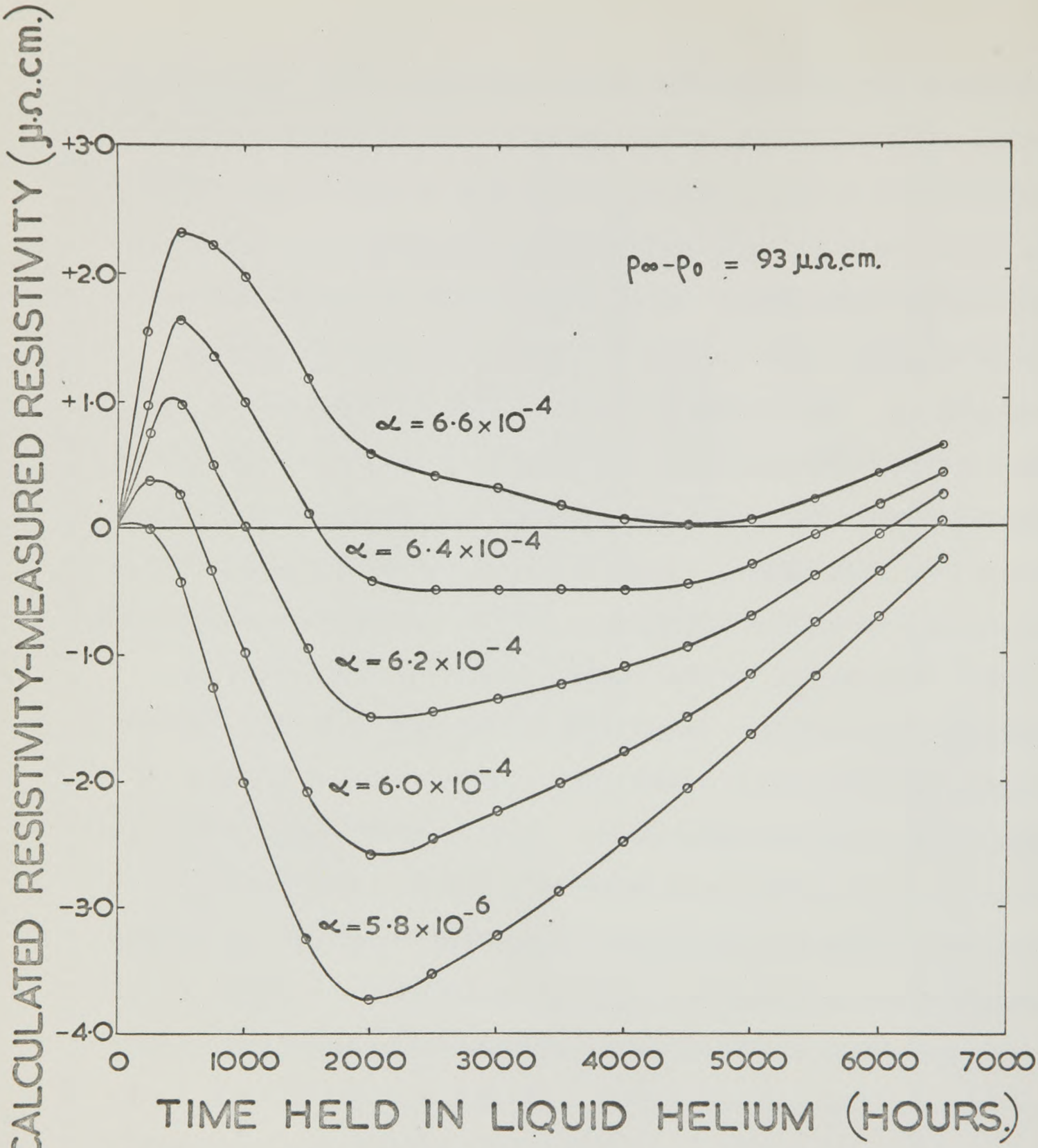


FIG.3.15. THE EFFECT OF VARIATION OF THE COEFFICIENT α IN THE FORMULA $\rho_s = (\rho_\infty - \rho_0)(1 - \exp -\alpha t)$ ON THE DEGREE OF AGREEMENT BETWEEN MEASURED AND CALCULATED RESISTIVIES OF . Pu. 5.

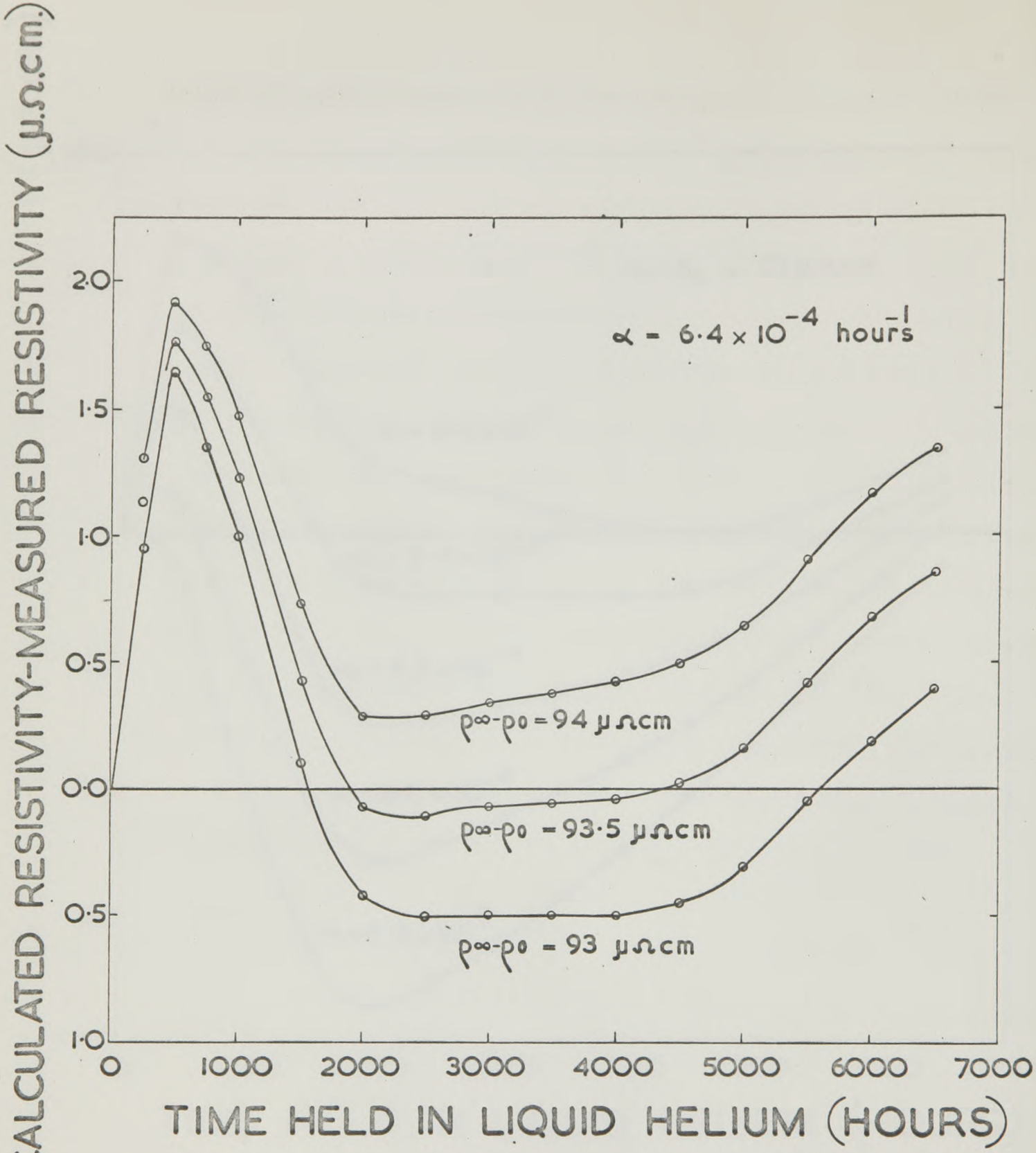


FIG. 3 .16. THE EFFECT OF VARIATION OF THE COEFFICIENT $(\rho_\infty - \rho_0)$ IN THE FORMULA $\rho_s = (\rho_\infty - \rho_0)(1 - \exp -\alpha t)$ ON THE DEGREE OF AGREEMENT BETWEEN MEASURED AND CALCULATED RESISTIVITIES OF Pu. 5.

of the asymptote is doubtful but it is probably slightly higher for Pu. 6 than for Pu. 5.

If the additional resistivity due to self damage were found to obey the law $\rho_a = (\rho_\infty - \rho_o)(1 - e^{-\alpha t})$ it would be possible to fit the experimental points to a curve of this form once the values of ρ_∞ and ρ_o had been determined. In Fig. 3.15 the difference between the calculated and measured resistivities is shown as a function of time, assuming that $\rho_\infty - \rho_o$ is 93 $\mu\Omega$ cm. and varying α from 5.8 to 6.6 x 10^{-4} hours^{-1}. The best fit would apparently be $\alpha = 6.4 \times 10^{-4}$ hours^{-1}, but this gives calculated values a few percent too high for the first ~1,700 hours, and increasingly too high after ~5,600 hours. In Fig. 3.16, with $\alpha = 6.4 \times 10^{-4}$, the effect of varying $\rho_\infty - \rho_o$ from 93 to 94 $\mu\Omega$ cm. is shown. The general form of the difference curve is unaltered but the fit is somewhat improved for $\rho_\infty - \rho_o = 93.5$ $\mu\Omega$ cm.

Now if $\rho_a = (\rho_\infty - \rho_o)(1 - e^{-\alpha t})$ ——— 3.i.

then $\frac{d\rho_a}{dt} = \alpha(\rho_\infty - \rho_o)\, e^{-\alpha t}$ ——— 3.ii.

and at $t = o$ $\left.\frac{d\rho_a}{dt}\right|_o = \alpha(\rho_\infty - \rho_o)$ ——— 3.iii.

thus $$\frac{\left.\frac{d\rho_a}{dt}\right|_t}{\left.\frac{d\rho_a}{dt}\right|_o} = \frac{\alpha(\rho_\infty - \rho_o)\, e^{-\alpha t}}{\alpha(\rho_\infty - \rho_o)} = e^{-\alpha t}$$ ——— 3.iv.

hence $$\log_e\left(\frac{\left.\frac{d\rho_a}{dt}\right|_t}{\left.\frac{d\rho_a}{dt}\right|_o}\right) = -\alpha t$$ ——— 3.v.

thus a plot of $\log_e\left(\frac{\text{slope at } t}{\text{slope at } t = o}\right)$ versus t should give

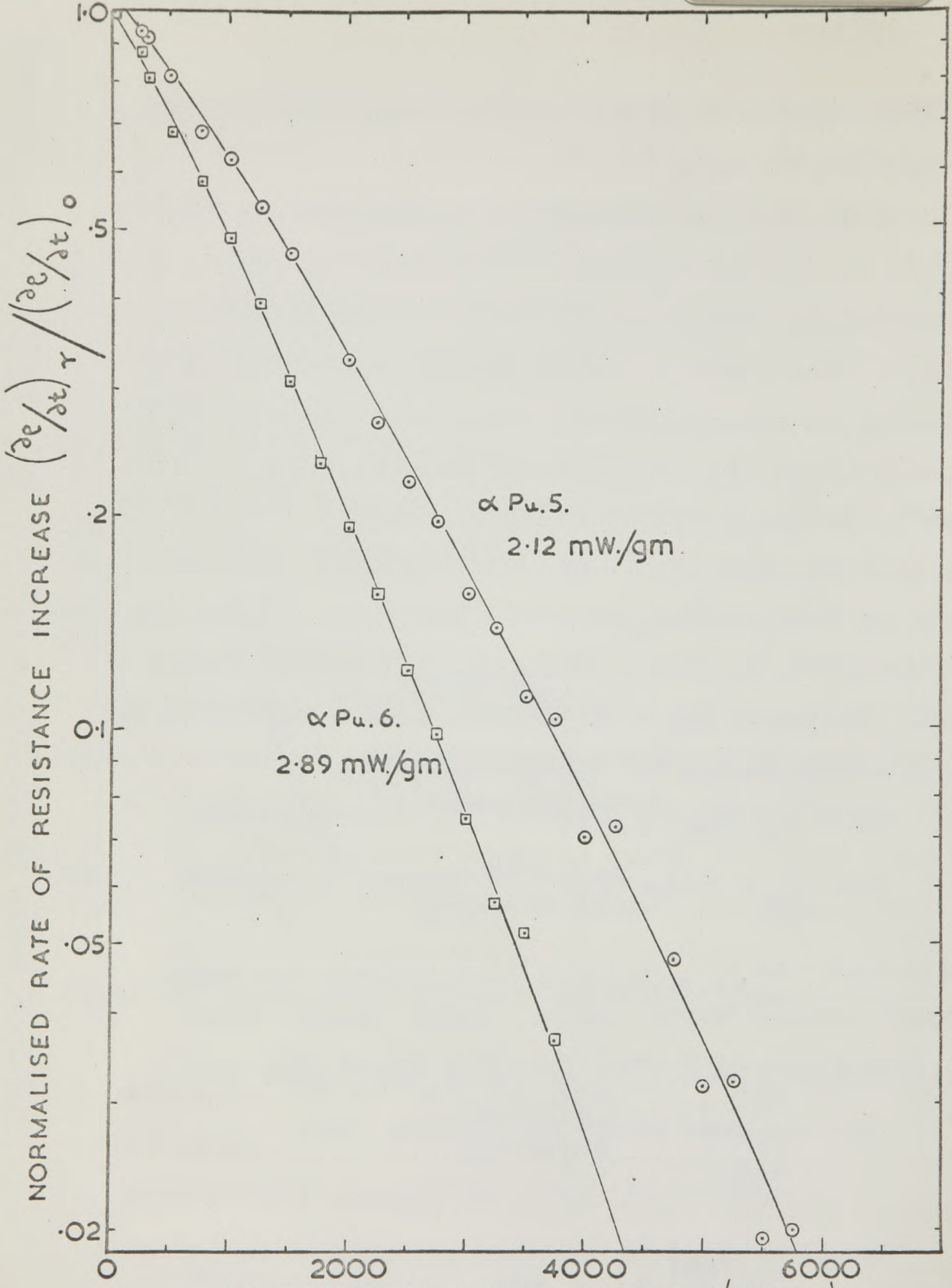


FIG.3.17. NORMALISED RATES OF RESISTANCE INCREASE FOR TWO SAMPLES OF ALPHA PLUTONIUM

a straight line of slope $-\alpha$.

In Fig. 3.17 such a plot is shown for both Pu. 5 and Pu. 6 and although there is a relationship between log $\left(\frac{\text{slope at } t}{\text{slope at } t = o}\right)$ and t, it is not simply linear. In fact α apparently increases from $\sim 3.4 \times 10^{-4}$ hours^{-1} at t = o to $\sim 7.9 \times 10^{-4}$ hours^{-1} at t = 5000 hours for Pu. 5. A similar apparent change is obtained for Pu. 6. This data is also given in Table 3.H.

Thus to summarise briefly, the relationship $\rho_a = (\rho\infty - \rho_o)(1-e^{-\alpha t})$ describes the form of the build in curves of Pu. 5 and Pu. 6 to within a few percent of the value of ρ_a. The discrepancies observed can be due to one or more of the following causes.

1) A change in the factor α, which we consider unlikely as α should be inversely proportional to the self heat, which itself should not change.

2) A secondary process occurring initially which has the effect of reducing the rate of resistivity increase for the first $\sim$ 1,500 hours. No obvious confirmation of this effect can however be found.

3) A secondary process, possibly one which reduces the value of $\rho\infty$, which becomes more efficient at reducing the measured value of the resistivity as ρ_m tends to $\rho\infty$.

Possible confirmation for the third hypothesis comes from a closer examination of the build in data of Fig. 3.14. Despite the unreliability of the results, the resistivity of Pu. 6 could be said to reach a shallow maximum at about t = 5,300 and the resistivity of Pu. 5 at $\sim$ t = 6,900 hours. However a closer examination of the results for Pu. 5 shown in Fig. 3.18. indicates that at t = 6,800 hours the scatter of the results increases markedly. Although a smooth curve can be drawn through the measured points, it is also possible to draw a series of short lines

TABLE 3.H.

Comparison of rates of resistivity increase of α Pu5 and α Pu6

	α Pu. 5		α Pu. 6	
Irradiation Time (hours)	$d\rho/dt$ ($\mu\Omega$cm/hr.10^3)	$\frac{(d\rho/dt)_T}{(d\rho/dt)_0}$	$d\rho/dt$ ($\mu\Omega$cm/hr.10^3)	$\frac{(d\rho/dt)_T}{(d\rho/dt)_0}$
0	53.00	1.000	70.75	1.000
250	49.50	.934	61.75	.873
500	43.05	.813	48.30	.681
750	36.45	.688	41.25	.583
1000	33.05	.623	34.35	.485$_5$
1250	28.37	.535$_5$	28.05	.397
1500	22.34	.462	21.75	.307$_5$
1750	20.40	.385	16.65	.235
2000	17.35	.327	13.57	.192
2250	14.25	.269	10.94	.155
2500	11.73	.221	8.55	.121
2750	10.35	.195	6.92$_5$	.097$_9$
3000	8.20	.155	5.27$_5$	.074$_6$
3250	7.31$_5$	.138	4.02$_5$	.056$_9$
3500	5.84	.110	3.65	.051$_6$
3750	5.44	.103	2.58	.036$_5$
4000	3.71	.070	–	–
4250	3.83	.072$_3$	–	–
4500	3.03$_5$	.057$_3$	–	–
4750	2.51	.047$_4$	0.55	.007$_8$
5000	1.67$_5$	.031$_6$	–	–
5250	1.60$_5$	.032$_0$	–	–
5500	1.03	.019$_4$	–	–
5750	1.05$_5$	.020	(-0.05)	–
6000	0.71$_5$	.013$_5$	–	–
6250	0.54$_5$	.010$_3$	–	–
6500	0.65$_7$	.012$_4$	–	–

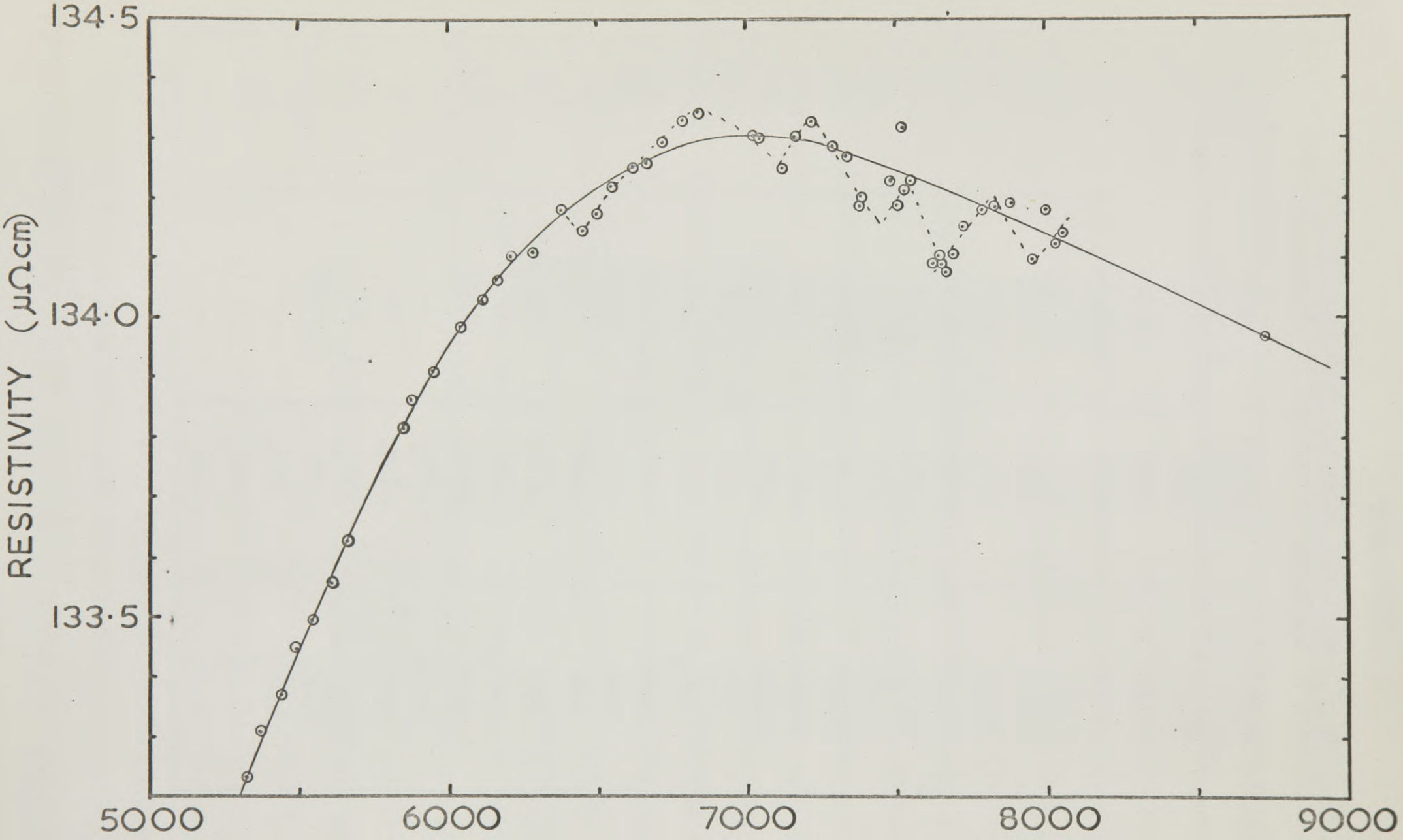


FIG.3.18 Pu5 POSSIBLE RESISTIVITY MAXIMUM

approximately parallel to the build in rate at ~ 6,800 hours. This would be justifiable if there was a slightly loose contact which was moving in a "stick and slip" fashion, giving small decreases in form factor followed by a lull in which the resistivity increased normally. Thus the existence of a genuine resistivity maximum is somewhat in doubt. No confirmatory run was attempted as the phenomenon is probably only of minor interest.

Lastly it is possible that self irradiation damage could, over the periods of time used in holding experiments, produce macroscopic changes in the dimensions of the specimen large enough to change its form factor. It would however require very sophisticated techniques to measure such a change to any degree of accuracy.

Thus although the resistivity increase due to self-damage, ρ_a, does not perfectly obey the law $\rho_a = (\rho_\infty - \rho_o)(1-e^{-\alpha t})$ ——— 3.i. it does provide a useful working approximation. We found earlier that for an exponential build in of this type we had the result

$$\log_e \left(\frac{\left.\frac{d\rho_a}{dt}\right|_t}{\left.\frac{d\rho_a}{dt}\right|_o} \right) = -\alpha t \qquad \text{——————} \quad 3.v.$$

Hence for two specimens of coefficients α_1 and α_2 respectively, which obey this relationship, the slopes of the graphs obtained by plotting $\log_e \left(\frac{\text{slope at } t}{\text{slope at } t=o} \right)$ against t would be proportional to α_1 and α_2 respectively. Although the relationship does not hold perfectly for Pu. 5 and Pu. 6 it is interesting to compare the gradients of the curves in Fig. 3.17 at the same values of the normalised slope ratio $\left(\text{slope } t / \text{slope } t=o\right)$. These are shown in Table 3.I.

TABLE 3.I.

Normalised Slope	Gradient α_6 (Pu. 6)	Gradient α_5 (Pu. 5)	Ratio Gradient α_6/α_5
0.8	7.24×10^{-4} hour^{-1}	4.95×10^{-4} hour^{-1}	1.46
0.6	7.68 "	5.83 "	1.32
0.4	8.70 "	6.56 "	1.34
0.2	9.44 "	7.07 "	1.34
0.1	9.70 "	7.33 "	1.32
0.0_5	10.33 "	7.84 "	1.32

Self Heat Pu. 6 = 2.894 mW/gm. Self Heat Pu. 5 = 2.124 mW/gm.

S/heat Pu.6 / S/heat Pu.5 = 1.36

It can be seen that over most of the range considered there is very good agreement between the ratio of the coefficients α_5 and α_6 and the ratio of the self heats. This agreement makes it highly unlikely that the apparent change in the coefficients α is due to a change in such a fundamental property as the self heat.

Finally in this chapter we shall briefly reconsider the results of the 5,000 hour run on α Pu.2 which demonstrate one of the most important features of the increase in resistance in alpha plutonium during low temperature self irradiation. In Table 3.J. we give the resistivities measured on first cooling at $\sim$ 290, $\sim$ 77, $\sim$ 20 and $\sim 5^{\circ}$K together with the probable asymptotic values of the resistivities at $\sim 20^{\circ}$K and $\sim 5^{\circ}$K in the damaged state. It can thus be seen that the asymptotic resistivity measured at $\sim 5^{\circ}$K reaches a value of $\sim$ 141 $\mu\Omega$cm. some 18 $\mu\Omega$cm. lower than the maximum value initially measured on cooling the undamaged specimen.

TABLE 3.J.

Temperature (°K)	~ 290	~ 194	~ 77	~ 20	~ 5
Resistivity on first cooling ($\mu\Omega$ cm.)	148.87	154.12	158.94	67.02	47.23
Resistivity as $t \rightarrow \infty$ ($\mu\Omega$ cm)	-	-	-	~141	~141

CHAPTER 4*

The Increase in Resistivity of Delta Stabilised Plutonium during Self-irradiation at Low Temperatures

It has already been stated that it is possible to retain the high temperature f.c.c. delta phase of plutonium to room temperature by alloying additions of suitable elements such as aluminium. The general form of the resistivity-temperature curves have been given by Meaden at low temperatures and King at higher temperatures (Lee, Hall, King and Meaden, 1960). These results show that as the aluminium content is raised from the minimum of 2.5 At.% required for stability to about 10 At.%, the residual resistivity increases from ~ 70 $\mu\Omega$ cm. to ~ 130 $\mu\Omega$ cm. At the same time the resistivity maximum moves to lower temperatures and the difference between the resistivity values at the maximum and at 0°K, ($\rho_{max} - \rho_0$), decreases.

After our initial holding run on α Pu. 1 in which we confirmed that the accumulation of self-irradiation damage at ~ 5°K caused a measurable increase in the resistivity, we decided to see if the same phenomena could be observed in δ stabilised plutonium. Accordingly a piece of 4 At.% Al. δ stabilised plutonium in the form of a sheet 6½ thou. thick was encapsulated to become sample Pu. 4. Details of this sample are

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*Part of the subject matter of this chapter has been published in papers by Lee, J.A., Mendelssohn, K. and Wigley, D.A. (Cryogenics 2 183 (1962) and Acta. Met. (to be published).

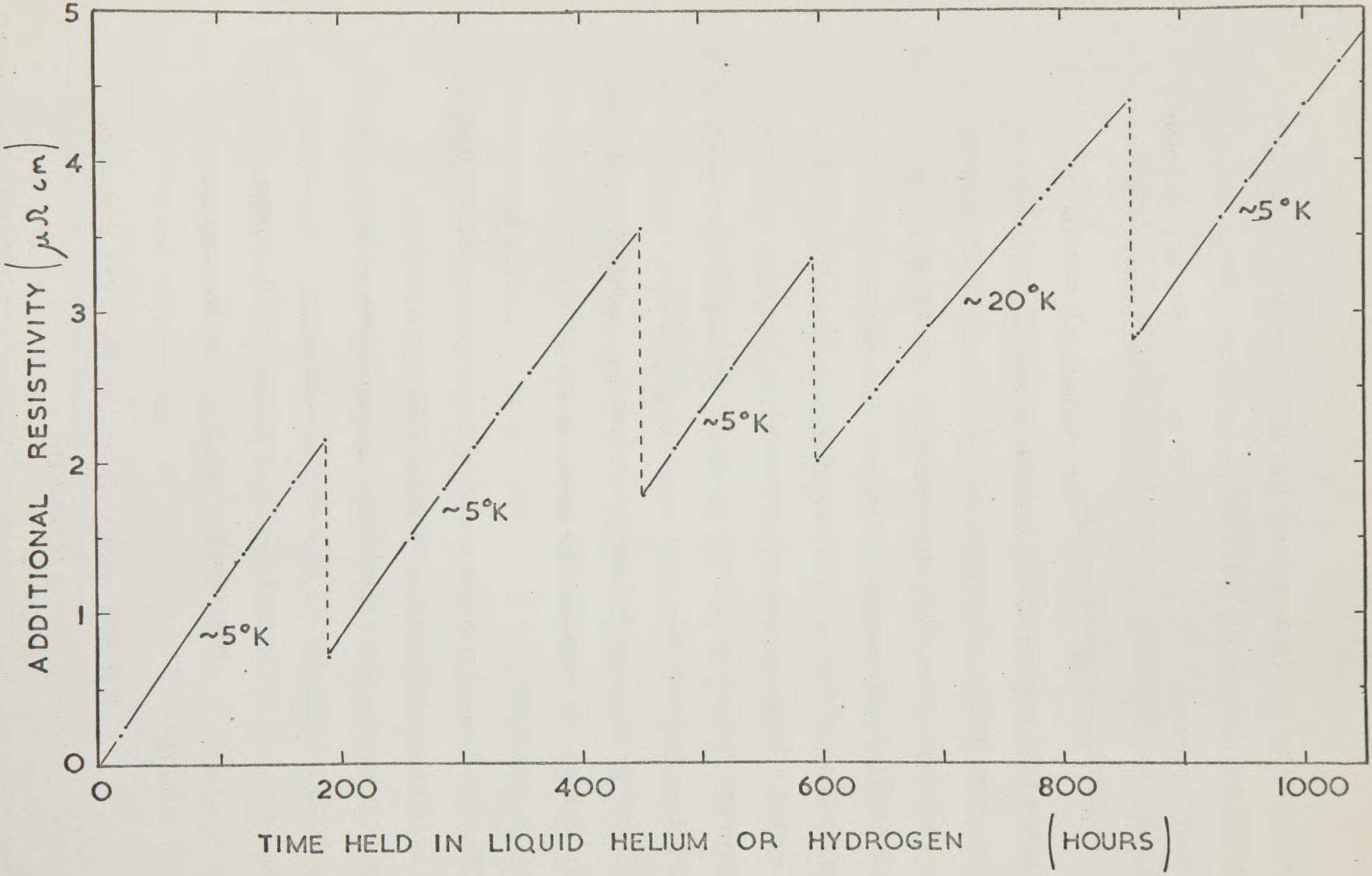


FIG. 4.1. FIRST HOLDING RUN ON δPu 4 SHOWING ANNEALING DURING TRANSFER

given in Appendix I. (Rolled sheet was used instead of a machined or extruded rod as in every other specimen, because it was the only stabilised plutonium available at the time, having been prepared for Hall effect work.) The resistivity was measured at ~ 290, ~ 273, ~ 194, ~ 87, ~ 77, ~ 20, and ~ 5°K on cooling and then as a function of time held in liquid helium. An initial rate of resistivity increase of 0.012 $\mu\Omega$ cm./hour was found, in contrast to an initial rate of 0.0525 $\mu\Omega$ cm./hour obtained from a sample of α plutonium made from the same stock. This serious discrepancy made further holding experiments desirable but at the time there was no syphon available to transfer liquid helium from one Dupree-Swift to another. The specimens were therefore physically transferred from one dewar to the other. This system worked tolerably well for α-plutonium specimens but, as Fig. 4.1 shows, about 50% of the resistivity increase in δ plutonium was lost during each transfer, although the specimen was not out of liquid helium for more than about 10 seconds. This difference in annealing behaviour of α and δ stabilised plutonium was later confirmed when the more careful experiments described in Chapter 5 were performed.

Fig. 4.1. also shows that there was apparently a slight decrease in the rate of resistivity increase as the irradiation time increased. Furthermore the rate of resistivity increase at ~ 20°K, 0.0092 $\mu\Omega$ cm/hr. was less than that at ~ 5°K, 0.011 $\mu\Omega$ cm./hr., for the same amount of additional resistivity, ~ 2.5 $\mu\Omega$ cm. We would not put too much reliance on these results in case they were falsified by the large degree of annealing which occurred during transfers.

Once a transfer syphon had been obtained, very long self-irradiation

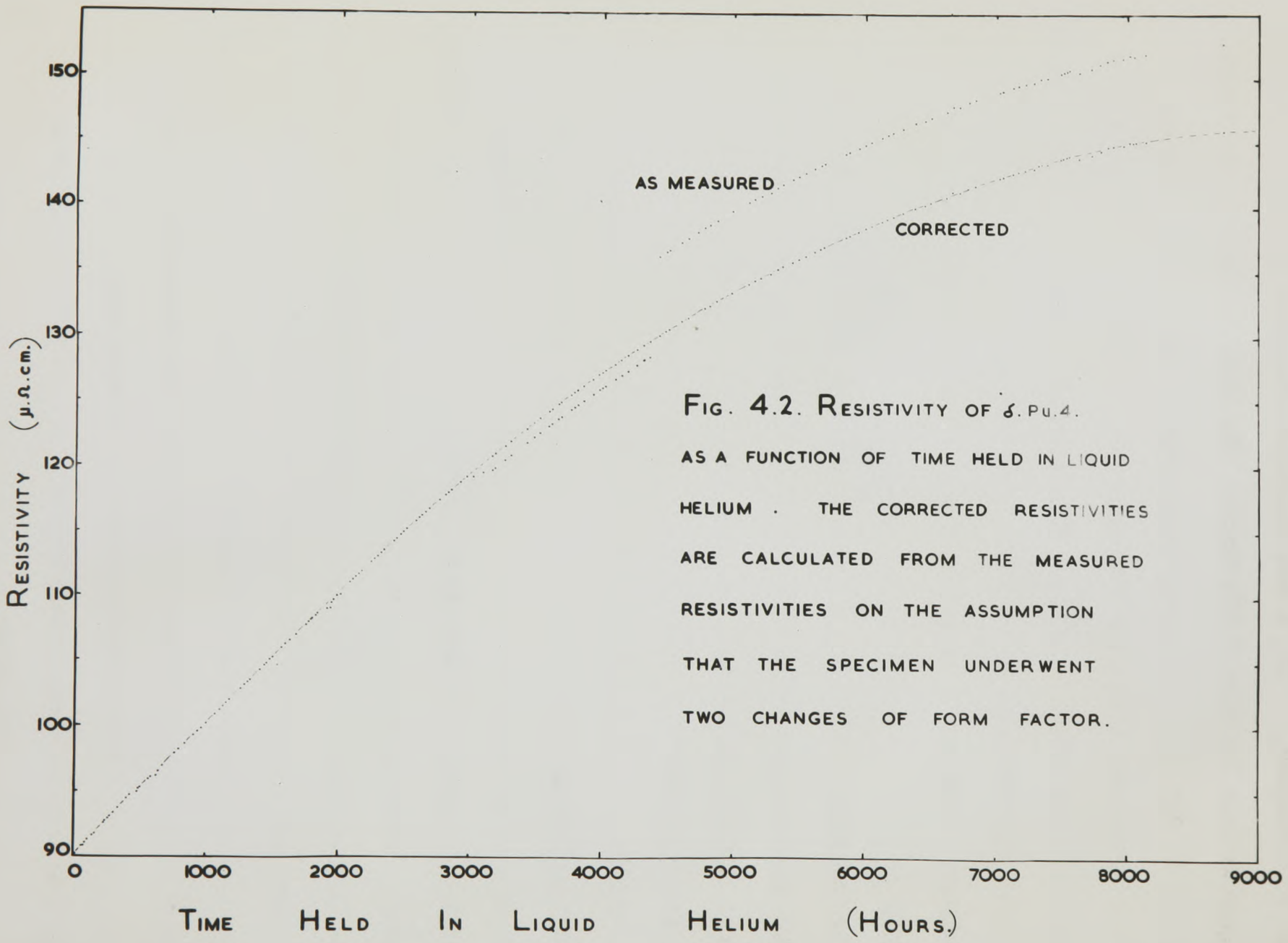


FIG. 4.2. RESISTIVITY OF δ. Pu.4. AS A FUNCTION OF TIME HELD IN LIQUID HELIUM. THE CORRECTED RESISTIVITIES ARE CALCULATED FROM THE MEASURED RESISTIVITIES ON THE ASSUMPTION THAT THE SPECIMEN UNDERWENT TWO CHANGES OF FORM FACTOR.

periods in liquid helium became possible. After prolonged annealing at room temperature, 6 Pu. 4 was therefore recooled to ~ 5°K and held in liquid helium for over 8,000 hours. The results of this experiment are shown in Fig. 4.2. Two curves are shown, one for the measured resistivity and the other for the corrected resistivity, both as a function of time held at ~ 5°K. The measured resistivity can be seen to undergo two reasonably abrupt changes in value at ~ 3,000 hours and 4,400 hours. We consider that there are two possible reasons for these changes:

a) They represented a genuine change in resistivity of the material.

b) The apparent change in resistivity was caused by a change in the measured resistance due to a change in the geometry of the specimen and hence the form factor.

Bearing in mind the fact that the specimen was very thin and lightly supported, we consider that the second reason is the more probable, especially as on both occasions the changes occurred immediately after fresh liquid helium had been transferred into the dewar containing the specimen. Thus if a change in form factor was responsible for the change in the measured resistance and hence for the apparent change in the resistivity, it should be possible to evaluate the true resistivity by finding the change in form factor. This was done by extrapolating the smooth curves obtained before and after the discontinuities and comparing the measured resistivities at a common time. Then:

$$(\text{Measured resistance} \times \text{form factor})_{\text{before}} = \text{true resistivity} = (\text{Measured resistance} \times \text{form factor})_{\text{after}}$$

The form factor was found to change from 1.47×10^{-3}cm. to 1.48336×10^{-3}cm. at the first discontinuity and from 1.48336×10^{-3}cm. to 1.40453×10^{-3}cm.

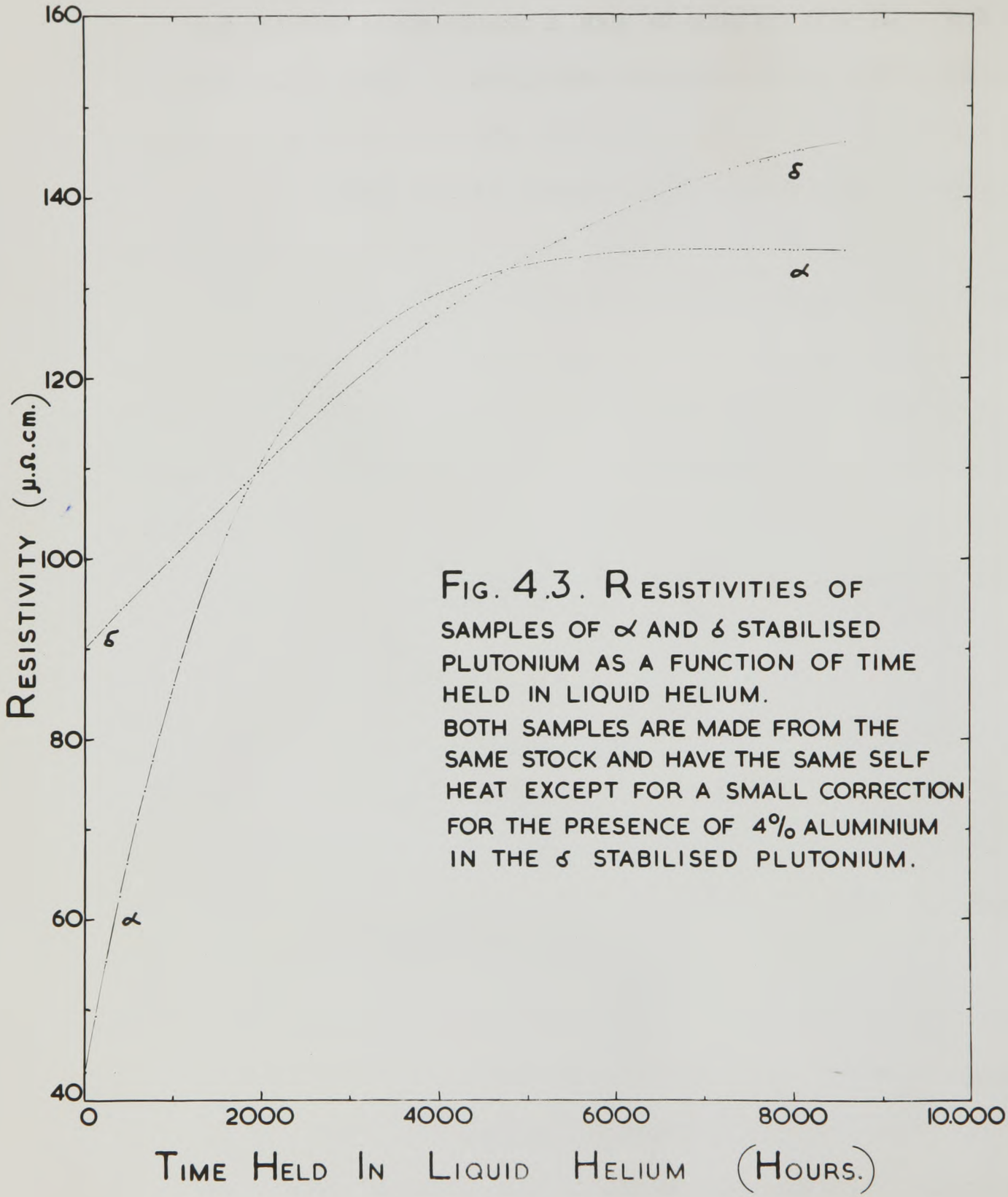


FIG. 4.3. RESISTIVITIES OF SAMPLES OF α AND δ STABILISED PLUTONIUM AS A FUNCTION OF TIME HELD IN LIQUID HELIUM.
BOTH SAMPLES ARE MADE FROM THE SAME STOCK AND HAVE THE SAME SELF HEAT EXCEPT FOR A SMALL CORRECTION FOR THE PRESENCE OF 4% ALUMINIUM IN THE δ STABILISED PLUTONIUM.

at the second. The corrected resistivity thus obtained is shown in Fig. 4.2. and will be seen to give a smooth curve through the discontinuities in the measured resistance. There is no change of slope as might have been expected had the discontinuity been caused by anything other than a simple change of form factor.

We are therefore confident that the corrected resistivity may justifiably be interpreted as the true resistivity, apart from the usual reservations imposed by the uncertainty in the absolute value of the form factor. The most important feature of the results shown in Fig. 4.2. is the asymptotic value of the resistivity at ~ 5°K in the damaged state compared with the values of the resistivity on first cooling. These are given in Table 2.A.

TABLE 2.A.

Temperature (°K)	~ 290	~ 194	~ 77	~ 20	~ 5
Resistivity on first cooling ($\mu\Omega$ cm.)	117.32	120.36	114.04	93.24	89.55
Resistivity as $t \rightarrow \infty$ ($\mu\Omega$ cm)	-	-	-	-	150 to 155

It can be seen that after an infinitely long period at ~ 5°K the resistivity would rise to a value of between 150 and 155 $\mu\Omega$ cm., some 30 $\mu\Omega$ cm. higher than its undamaged maximum of ~ 122 $\mu\Omega$ cm. at ~ 140°K. This is in direct contrast to the results obtained with α plutonium in which the asymptotic 5°K resistivity was between 140 and 145 $\mu\Omega$ cm., some 18 $\mu\Omega$ cm. lower than the 105°K maximum of 158 to 163 $\mu\Omega$ cm.

The other striking difference between the self damage behaviour of

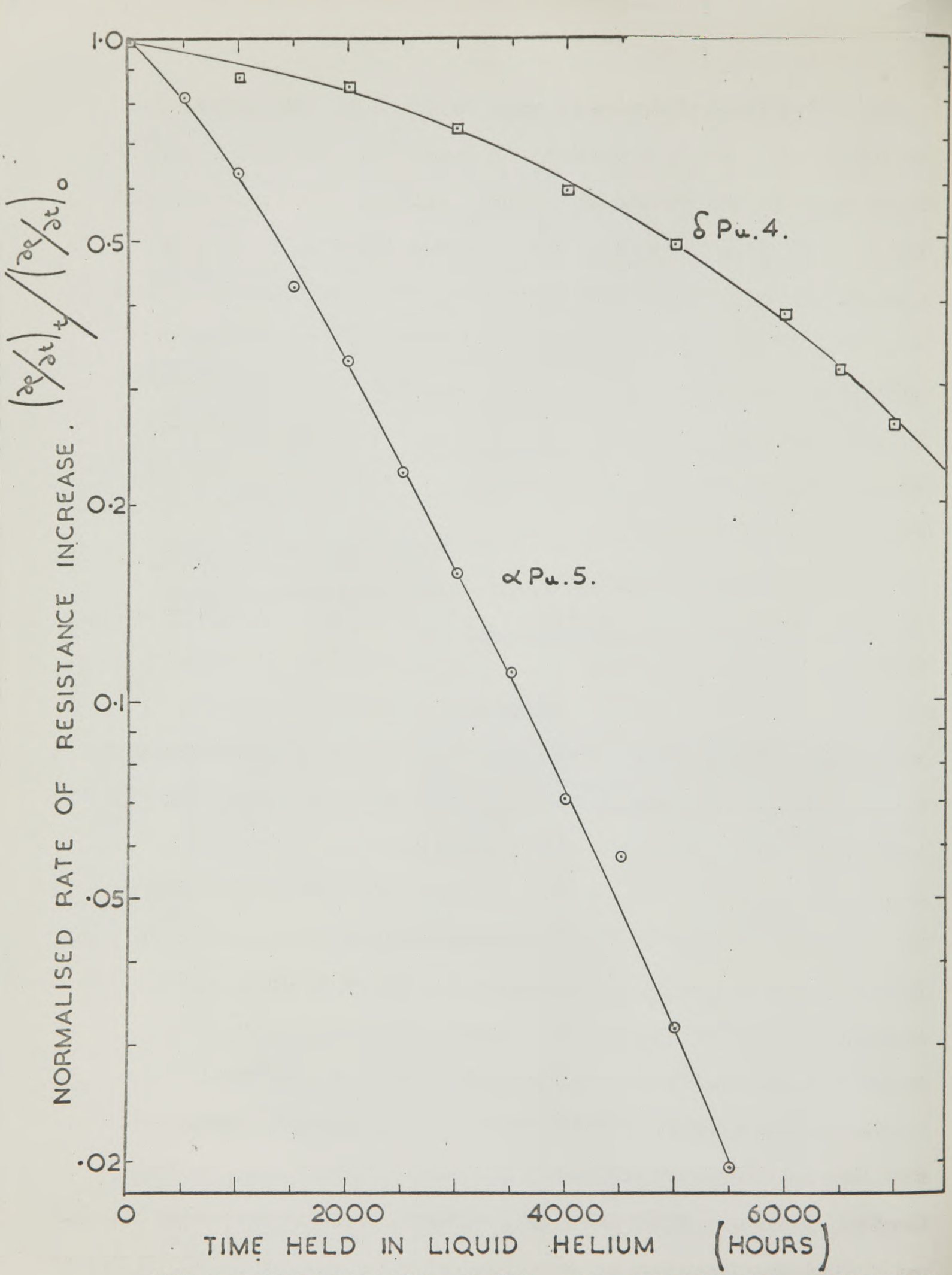


FIG. 4.4. NORMALISED RATES OF RESISTANCE INCREASE FOR ALPHA AND DELTA STABILISED PLUTONIUM.

α and δ stabilised plutonium is shown in Fig. 4.3. The corrected resistivity of δ Pu. 4 is plotted as a function of time held in liquid helium as is the resistivity of α Pu.5. Both specimens were prepared from the same stock and so have the same basic self-heat apart from a small correction for the 4 At.% Aluminium in the δ specimen. It can be seen that whereas α Pu.5 had reached its maximum (?) value after about 7,000 hours, the resistivity of δ Pu. 4 was still increasing steadily. Thus not only does δ stabilised plutonium have a smaller initial rate of resistivity increase than α plutonium, but it also takes considerably longer to reach its saturation value.

This point may be seen more clearly in Fig. 4.4. in which the normalised rates of resistance increase for the α and δ specimens are shown as a function of holding time. It was pointed out in Chapter 3 that a true exponential resistivity increase would lead to a linear relationship between $\log\left(\frac{\text{rate at } t = t}{\text{rate at } t = 0}\right)$ and holding time, t. From the non-linearity of both plots in Fig. 4.4. it is obvious that the build in is not a pure exponential, the δ results proving perhaps even less well behaved. Thus it is not possible to obtain a unique value of the coefficient α in the formula $\rho_a = (\rho_\infty - \rho_0)(1 - e^{-\alpha t})$ from the slope of the curves in Fig. 4.4. However it may be instructive to compare the slopes of the curves for the same value of normalised rate of resistivity increase, say at 0.5. The values thus obtained for the coefficient α are 5.46×10^{-4} hours^{-1} for δ Pu. 4 and 14.75×10^{-4} hours^{-1} for α Pu. 5. (The slopes measured from Fig. 4.4. have been multiplied by 2.303 to convert $\log_{10}$ to $\log_e$.) The measured values of the rates of resistivity increase from which Fig. 4.4. was plotted are also given in Table 2.B. Possible reasons for the difference

in the build in rate coefficient α between α and δ stabilised plutonium will be discussed in the final chapter.

TABLE 2.B.

Self Irradiation Damage in α and δ Plutonium

	Pu. 5		Pu. 4		
Time hours	Slope ($\mu\Omega$cm/hr.10^3)	Slope t=t / Slope t=o	Slope ($\mu\Omega$cm/hr.10^3)	Corrected Slope ($\mu\Omega$cm/hr.10^3)	Slope t=t / Slope t=o
0	52.5_0	1.00	11.45	11.45	1.00
500	43.0_5	.820	-	-	-
1000	33.0_5	.629	10.02_5	10.02_5	.876
1500	22.3_4	.425	-	-	-
2000	17.3_5	.330	9.72_5	9.72_5	.849
2500	11.7_2	.223	-	-	-
3000	8.2_0	.156	8.46	8.46	.739
3500	5.8_4	.111	-	-	-
4000	3.7_1	.0706	6.72	6.78	.592
4500	3.0_{35}	.0578	-	-	-
5000	1.67_5	.0319	5.89	5.62_8	.491
5500	1.03	.0196	-	-	-
6000	0.71_5	.0136	4.60	4.39_5	.384
6500	0.657_5	.0125	3.77_5	3.60_7	.315
7000	-	-	-	3.04_4	.266

In Chapter 3 we described an experiment in which the temperature dependence of the additional resistivity caused by self damage in

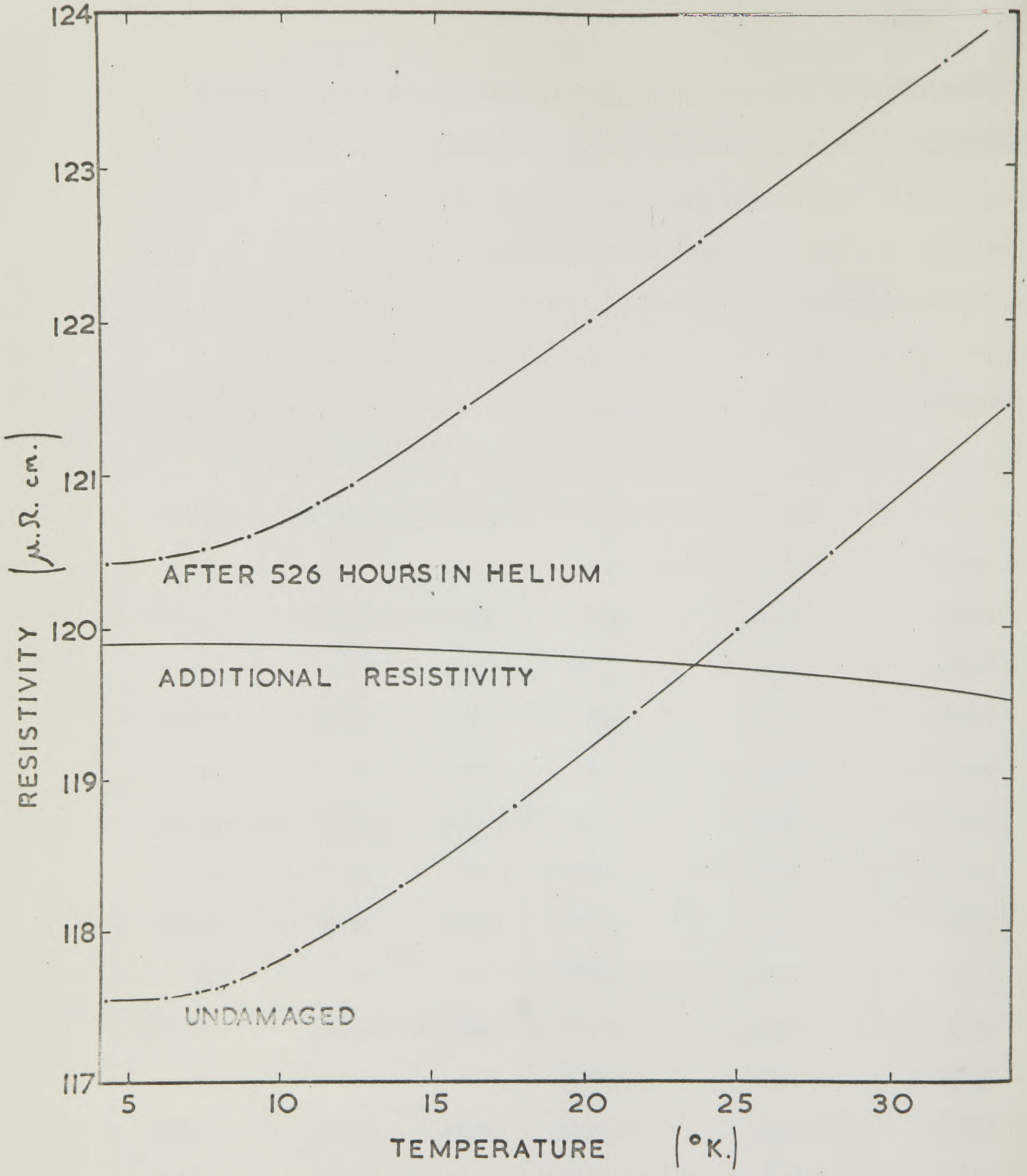


FIG. 4.5. TEMPERATURE DEPENDENCE OF THE ADDITIONAL RESISTIVITY CAUSED BY SELF IRRADIATION DAMAGE IN 8% Al. δ. STABILISED PLUTONIUM.

α plutonium was inferred from measurements of resistivity made in the undamaged and damaged states. This experiment was also performed on a specimen of δ plutonium stabilised by the addition of 8 At.% aluminium, Sample Pu. 12, and the results are shown in Fig. 4.5. Only one curve was obtained for the damaged state because the insulation between the lead wires failed shortly afterwards and the run was abandoned. No readings were taken at temperatures greater than $\sim 32^{\circ}K$ in the damaged state because it was known that annealing set in at $\sim 35^{\circ}K$ in δ stabilised plutonium, a somewhat lower temperature than for α plutonium. It would appear from Fig. 4.5. that the additional resistivity produced by self-irradiation damage, $\Delta\rho$, is less temperature dependent in δ stabilised plutonium than in α plutonium. It is, however, important to compare the temperature dependence of $\Delta\rho$ at comparable damage concentrations, as re-examination of either Fig. 3.5 or Fig. 3.6 will show that $\Delta\rho$ becomes more temperature dependent as the specimen becomes more damaged.

Now 526 hours self-irradiation in liquid helium causes the resistivity measured at $\sim 5^{\circ}K$ of the δ specimen to increase from ~ 117.54 to ~ 120.42 $\mu\Omega$cm., which is about the same increase as would have been obtained by raising the temperature of the undamaged specimen from $\sim 5^{\circ}K$ to $\sim 28^{\circ}K$. Similarly from Fig. 3.6, 647 hours self-irradiation of α Pu.9 produces the same resistivity increase as does raising the temperature from ~ 5 to $\sim 28^{\circ}K$. (The temperature $28^{\circ}K$ has no physical significance and was chosen simply for convenience.) Alternatively we could compare the temperature dependence of $\Delta\rho$ for the same concentration of defects. Using the simplest assumptions the number of defects produced in a given time should be proportional to the self heat of the sample. As the self

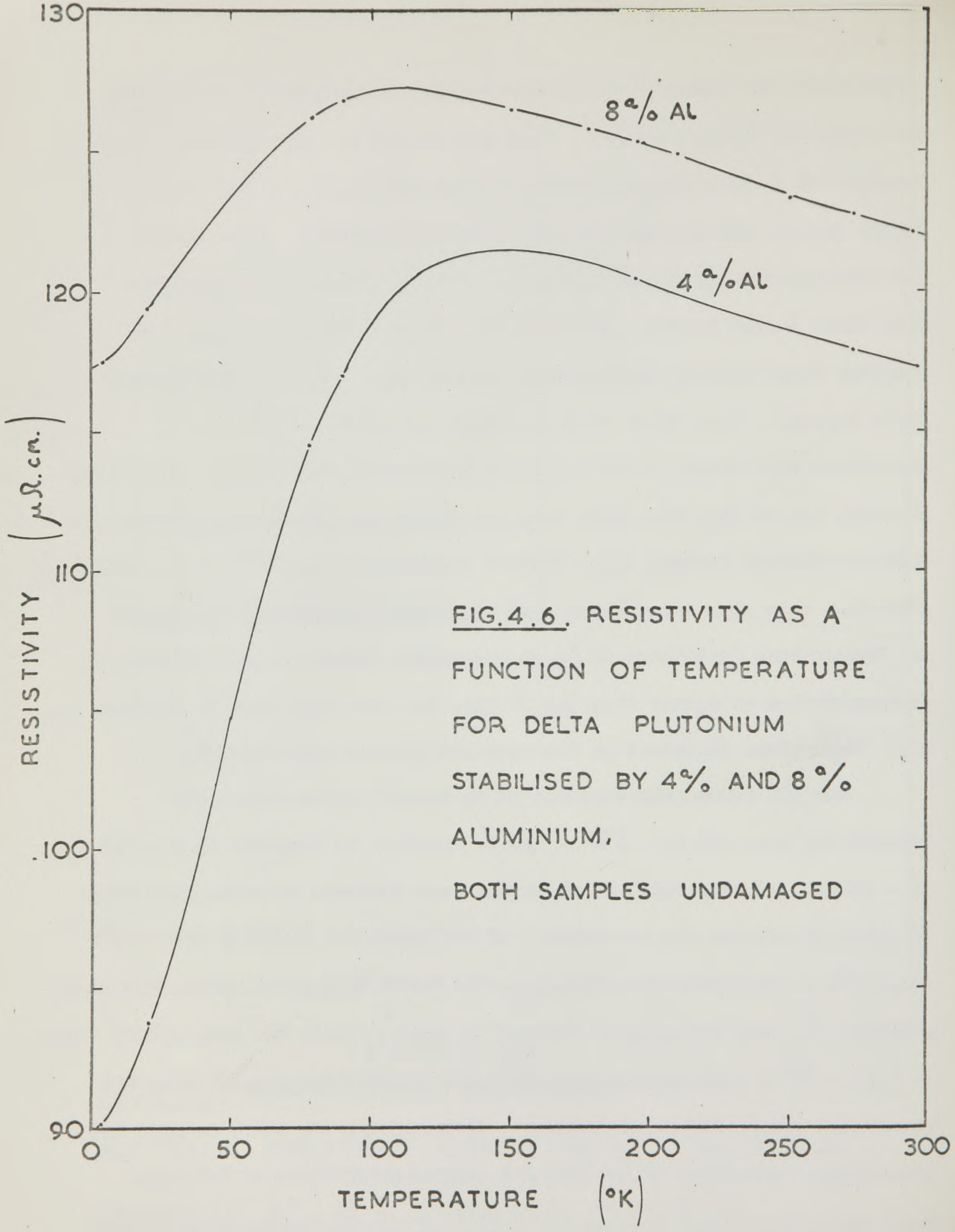
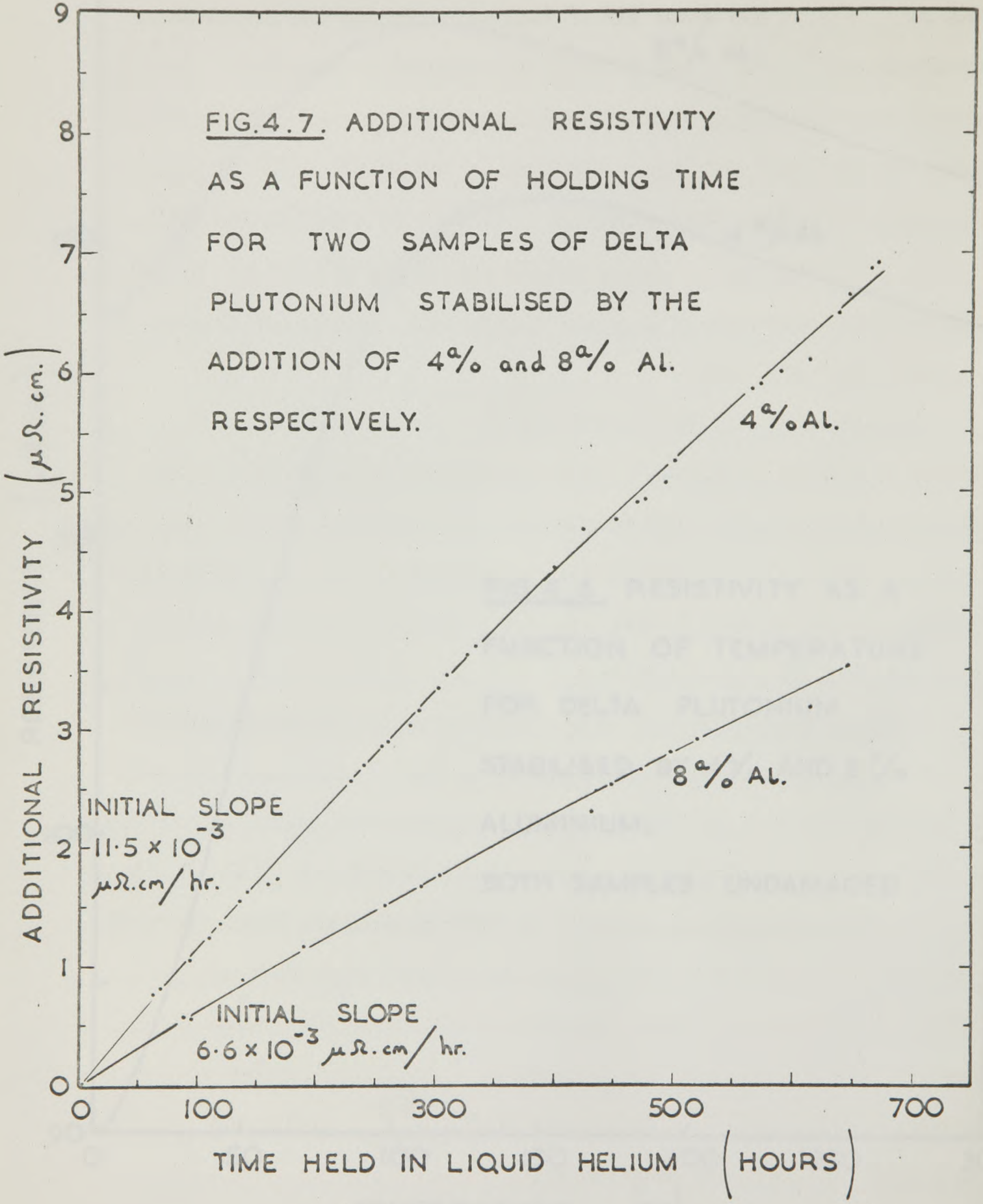


FIG. 4.6. RESISTIVITY AS A FUNCTION OF TEMPERATURE FOR DELTA PLUTONIUM STABILISED BY 4% AND 8% ALUMINIUM, BOTH SAMPLES UNDAMAGED


FIG.4.7. ADDITIONAL RESISTIVITY AS A FUNCTION OF HOLDING TIME FOR TWO SAMPLES OF DELTA PLUTONIUM STABILISED BY THE ADDITION OF 4% and 8% Al. RESPECTIVELY.
4% Al.
8% Al.
INITIAL SLOPE 11·5 × 10⁻³ μΩ.cm/hr.
INITIAL SLOPE 6·6 × 10⁻³ μΩ.cm/hr.
ADDITIONAL RESISTIVITY (μΩ.cm.)
TIME HELD IN LIQUID HELIUM (HOURS)
0
1
2
3
4
5
6
7
8
9
0
100
300
500
700

heat of δ Pu. 12 was about 72% of that of α Pu. 9, the temperature dependence of $\Delta\rho$ for α Pu. 9 should be compared to that for δ Pu. 12 after a correspondingly shorter self-irradiation period. Using either method we find that for the α specimen $\Delta\rho$ drops to ~ 60% of its 5°K value on raising the temperature to ~ 34°K. In contrast the value of $\Delta\rho$ at ~ 34°K was, for δ Pu. 12, still 88% of its 5°K value. Deviations from Matthiessen's rule thus appear greater in α plutonium than in δ stabilised plutonium.

It was shown by Meaden and King that the difference (ρ max $-\rho_o$) decreased and the temperature of the resistivity maximum fell as the aluminium content of δ stabilised plutonium increased. This behaviour is shown for our two δ plutonium samples in Fig. 4.6. For the 4 At.% Al. specimen the difference (ρ max $-\rho_o$) is ~ 34.5 $\mu\Omega$cm. while it is ~ 10 $\mu\Omega$cm. for the 8 At.% specimen.

To see what effect, if any, variation of the aluminium content had on the rates of resistivity increase of our δ specimens when held at low temperatures, we compared the initial rates of resistance increase of the 4 At.% Al. and 8 At.% Al. specimens when held at ~ 5°K. In Fig.4.7 the additional resistivity produced by self-irradiation damage is shown as a function of the time held in liquid helium. In both cases the scatter on the measured values is quite large but smooth curves can be drawn through the majority of the points. The initial rates of resistivity increase are 6.6×10^{-3} $\mu\Omega$cm/hr. and 11.5×10^{-3} $\mu\Omega$cm/hr. for the 8 At.% and 4 At.% Al. specimens respectively.

It was, at one time, thought that the self irradiation damage induced resistivity increase in δ stabilised plutonium would saturate at

a value slightly smaller than the value of the resistivity maximum in the undamaged state. If then the build in followed a law of the form

$$\rho_a = (\rho_{max} - \rho_o)(1 - e^{-\alpha t}) \quad \text{——————} \quad 4.i.$$

the relationship $\left.\frac{d\rho}{dt}\right|_{t=0} = \alpha(\rho_{max} - \rho_o)$ —— 4.ii

would hold. For two specimens of δ stabilised plutonium with similar coefficients α, the relationship

$$\frac{\left.\frac{d\rho_1}{dt}\right|_{t=0}}{\left.\frac{d\rho_2}{dt}\right|_{t=0}} = \frac{(\rho_{max} - \rho_o)_1}{(\rho_{max} - \rho_o)_2} \quad \text{——} \quad 4.iii$$

would follow. Substituting the experimental values for the 4 At.% Al. and 8 At.% Al. specimens we obtained

$$\frac{\left.\frac{d\rho}{dt}_{(8At.\%)}\right|_{t=0}}{\left.\frac{d\rho}{dt}_{(4At.\%)}\right|_{t=0}} = \frac{6.6 \times 10^{-3}}{11.5 \times 10^{-3}} = 0.57_4$$

and $$\frac{(\rho_{max} - \rho_o)_{(8At.\%)}}{(\rho_{max} - \rho_o)_{(4At.\%)}} = \frac{10}{31.5} = 0.31_7$$

Thus the relation $\rho_a = (\rho_{max} - \rho_o)(1 - e^{-\alpha t})$ would not appear to hold as the inequality between the two sides of Eqn. 4.iii is much greater than that allowed by their slightly different self heats.

From Fig. 3.3 it can be seen that the asymptotic value of the 5°K resistivity of δ Pu. 4 was between 150 and 155 $\mu\Omega$ cm.

Assuming now a build in of the form

$$\rho_a = (\rho_\infty - \rho_o)(1 - e^{-\alpha t}) \quad \text{————} \quad 4.iv$$

we have $$\frac{\frac{d\rho_1}{dt}\Big|_{t=0}}{\frac{d\rho_2}{dt}\Big|_{t=0}} = \frac{\alpha_1(\rho_\infty - \rho_o)_1}{\alpha_2(\rho_\infty - \rho_o)_2} \qquad \text{---- 4.iv}$$

for two specimens 1 and 2.

then if: i) the coefficient α is about the same for the two specimens

ii) the value of ρ_∞ is similar for the two specimens

iii) the build in follows the above law reasonably well

we have

$$\text{L.H.S.} \quad \frac{6.6 \times 10^{-3}}{11.5 \times 10^{-3}} = .57_4$$

$$\text{R.H.S.} \quad \frac{(150 \text{ to } 155) - 117}{(150 \text{ to } 155) - 90} = \frac{33 \text{ to } 38}{60 \text{ to } 65} = .55 \text{ to } .585$$

$$= \underline{.572} \quad (\text{if } \rho_\infty = 153\ \mu\Omega\text{ cm.})$$

Thus to a very good approximation R.H.S. = L.H.S.

Let us therefore examine the implications of this relationship by reconsidering the assumptions made above.

Firstly, does equation 4.iv. really describe the build in of resistivity in δ stabilised plutonium ? If it does, the curve shown for δ Pu. 4 in Fig. 4.4. would be a straight line of slope equal to the rate coefficient α. As the curve is not a straight line equation 4.iv. cannot be strictly valid. However if two such curves were obtained for the 4 At.% Al. and 8 At.% Al. specimens such that $\alpha_{(4\%)} / \alpha_{(8\%)}$ = constant at all times, then the relationship between the rates of resistivity increase given in equation 4.v. would still be valid. As the two specimens were made from the same stock, their self heats are identical

except for a small correction due to the difference in their aluminium contents. If is therefore not unreasonable that the ratio of the coefficients $\alpha_{(4\%)}$ and $\alpha_{(8\%)}$ should be constant.

Secondly we have the assumption that the two specimens will have approximately the same asymptotic 5°K resistivity. This assumption was unfortunately not tested before our experimental work ceased. There is one interpretation of the behaviour of δ stabilised plutonium during self irradiation that would lead to this conclusion. If very long periods of low temperature self-irradiation could de-stabilise δ plutonium alloys, they would revert to very impure α plutonium. This α plutonium would then be so supersaturated with aluminium that the asymptotic ~ 5°K resistivity would be virtually independent of the aluminium content of the original δ alloy. Furthermore the asymptotic 5°K resistivity would then be expected to have a high value similar to the value of ~ 153 $\mu\Omega$ cm. observed for our 4 At.% δ specimen.

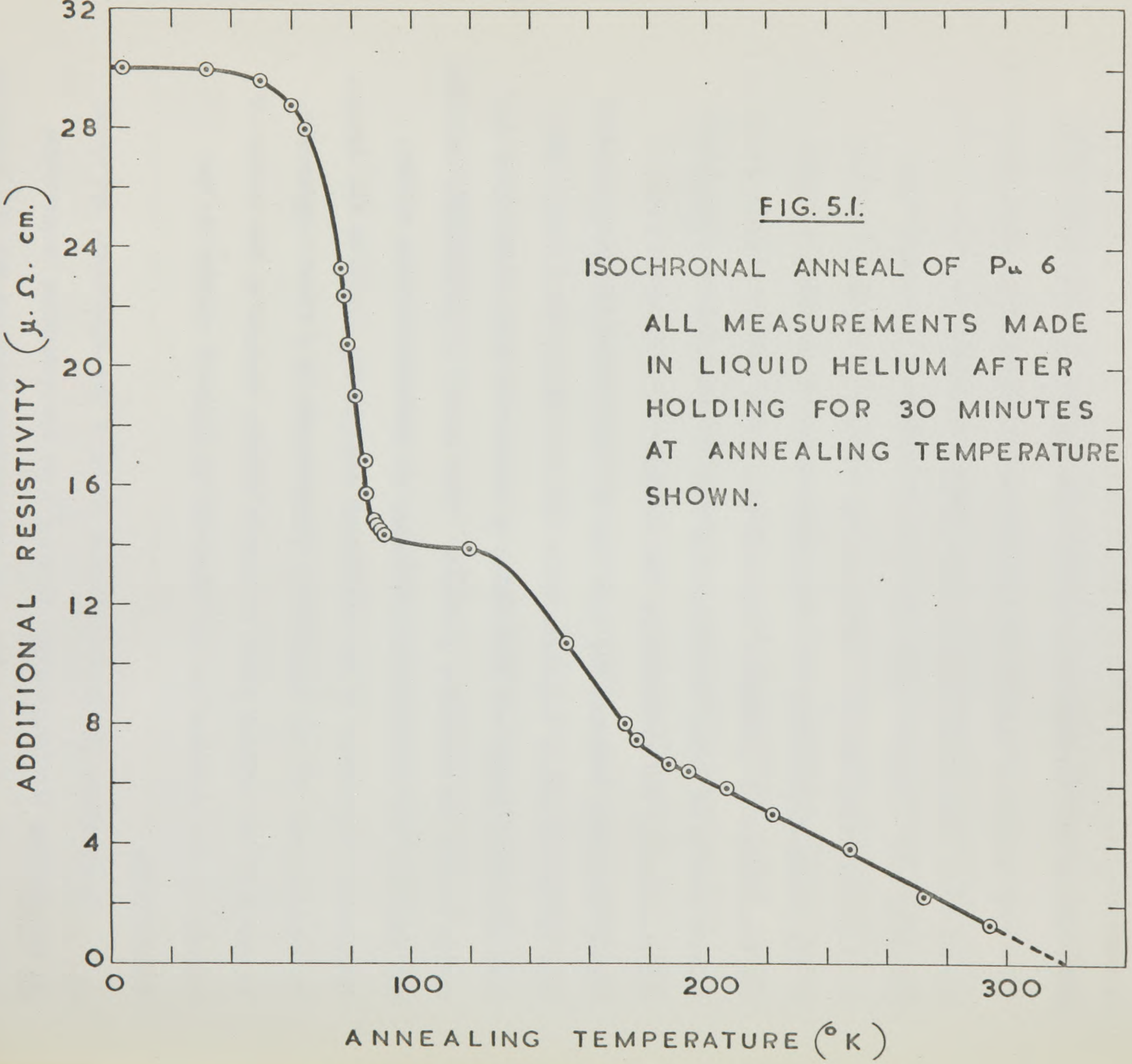
Further discussion of the behaviour of δ stabilised plutonium during self-irradiation will be left to the final chapter.

CHAPTER 5

Isochronal Annealing Behaviour of Alpha and Delta Stabilised Plutonium

The method of isochronal annealing is widely used to study the way in which damage produced by fast particle irradiation, or by quenching from a higher temperature, is recovered on warming. It involves measuring the resistivity of the damaged specimen at the end of its irradiation period at a convenient fixed temperature, raising the temperature as quickly as possible to a higher value, holding for a certain period of time, then quenching back to the original temperature and remeasuring the resistivity. The specimen is then raised to a higher annealing temperature, held for the same period of time, quenched back to the reference temperature and its resistivity remeasured. The main annealing stages are then shown by relatively large resistivity decreases during the annealing periods. This method is particularly suitable for studying the self-irradiation damage of plutonium because of the temperature dependence of the additional resistivity caused by the damage. By carrying out all the resistivity measurements at a fixed temperature, in our case the boiling point of liquid helium, changes in the number of defects in the specimen are not confused by apparent changes in the resistivity.

In practice the most difficult parts of the experiment are found to be; raising the temperature from $\sim 5^{\circ}K$ to the annealing temperature quickly enough and maintaining this temperature constant for the annealing period. The methods used for doing this were discussed in Chapter 2. An


ADDITIONAL RESISTIVITY (μ. Ω. cm.)
0
4
8
12
16
20
24
28
32
0
100
200
300
ANNEALING TEMPERATURE (°K)
FIG. 5.1.
ISOCHRONAL ANNEAL OF Pt 6
ALL MEASUREMENTS MADE IN LIQUID HELIUM AFTER HOLDING FOR 30 MINUTES AT ANNEALING TEMPERATURE SHOWN.

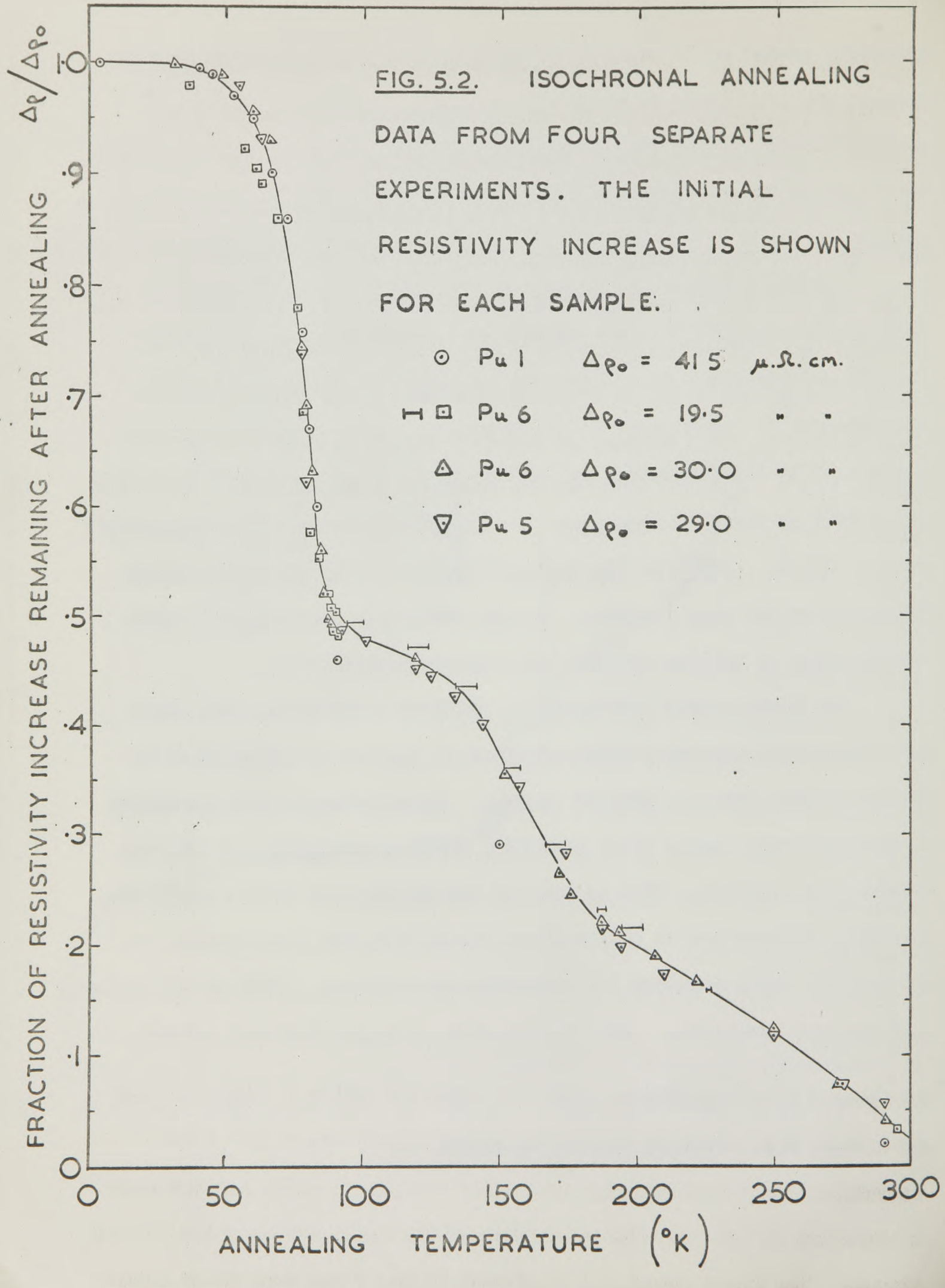
annealing period of 30 minutes was chosen instead of a shorter period because the time taken to reach the annealing temperature becomes proportionately larger for the shorter periods. In fact no corrections were applied for the time spent reaching the annealing temperature as in general it was less than 10% of the time spent at the annealing temperature.

The first Isochronal annealing experiment performed on Pu. 1 showed that approximately 50% of the additional resistivity was annealed by $\sim 80^{\circ}K$ and all but a few percent was annealed after warming to room temperature.* Refinement of the techniques used, especially in the range ~ 90 to ~ $300^{\circ}K$ showed the existence of a higher temperature stage at ~ $160^{\circ}K$ as shown in Fig. 5.1. It is unfortunate that the temperature range ~ 100 to ~ $180^{\circ}K$ is the most difficult in which to obtain steady temperatures for long periods. We are confident, however, that this second stage is genuine and not due to experimental error.

One experimental difficulty is peculiar to plutonium and other materials which undergo self-irradiation as opposed to irradiation by fast particles from an external source. In experiments with particles from an external source it is possible, within reason, to turn off the source when required. Then as long as the specimen is stored below its annealing temperature it will neither become more nor less damaged and may be left until required for annealing experiments. This is not so for self-damaged specimens. If, for example, a sample has been annealed in

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*This result was published in part of a paper by Lee, J.A., Mendelssohn, K., and Wigley, D.A., Physics Letters, 1 (1962)


FIG. 5.2. ISOCHRONAL ANNEALING DATA FROM FOUR SEPARATE EXPERIMENTS. THE INITIAL RESISTIVITY INCREASE IS SHOWN FOR EACH SAMPLE.
⊙ Pu 1 Δρ₀ = 41·5 μ.Ω.cm.
⊡ Pu 6 Δρ₀ = 19·5 " "
△ Pu 6 Δρ₀ = 30·0 " "
▽ Pu 5 Δρ₀ = 29·0 " "
FRACTION OF RESISTIVITY INCREASE REMAINING AFTER ANNEALING Δρ/Δρ₀
0 ·1 ·2 ·3 ·4 ·5 ·6 ·7 ·8 ·9 1·0
0 50 100 150 200 250 300
ANNEALING TEMPERATURE (°K)

stages from ~ 5°K to ~ 50°K during one working day it cannot simply be returned to liquid helium for storage overnight because it will accumulate more self damage. Furthermore defects of the type already annealed will build in more quickly than those as yet un-annealed and the additional resistivity produced overnight will not be representative of the un-annealed defects. This difficulty can be almost overcome by covering the temperature range ~ 5°K to ~ 100°K in one long day, which for the experiment shown in Fig. 5.1. involved 14 readings each taking over 3/4 hour. Then as long as the 80°K annealing stage has been fully annealed it is possible to leave the specimen in liquid oxygen or liquid nitrogen overnight with very little or no further build in or annealing occurring. Finally by allowing the specimens to self damage for a few weeks prior to annealing, the resistivity stored will be so much greater than that which could be stored overnight in liquid oxygen that any corrections needed will be very small.

Further annealing experiments were carried out in order to improve the resolution of the annealing peaks and also to see if there was any strong dependence on the amount of resistivity stored prior to annealing. The results of four such experiments are shown in Fig. 5.2. in which the fraction of the resistivity increase remaining after annealing is shown as a function of annealing temperature. In the Key to the figure the value of the additional resistivity prior to annealing is shown for each specimen. Within the small range of resistivities used it is impossible to detect any strong dependence on radiation dose, repetition under more closely controlled conditions might however show a variation in the relative magnitudes of the first and second annealing stages. The first experiment performed on Pu. 6 was done under rather

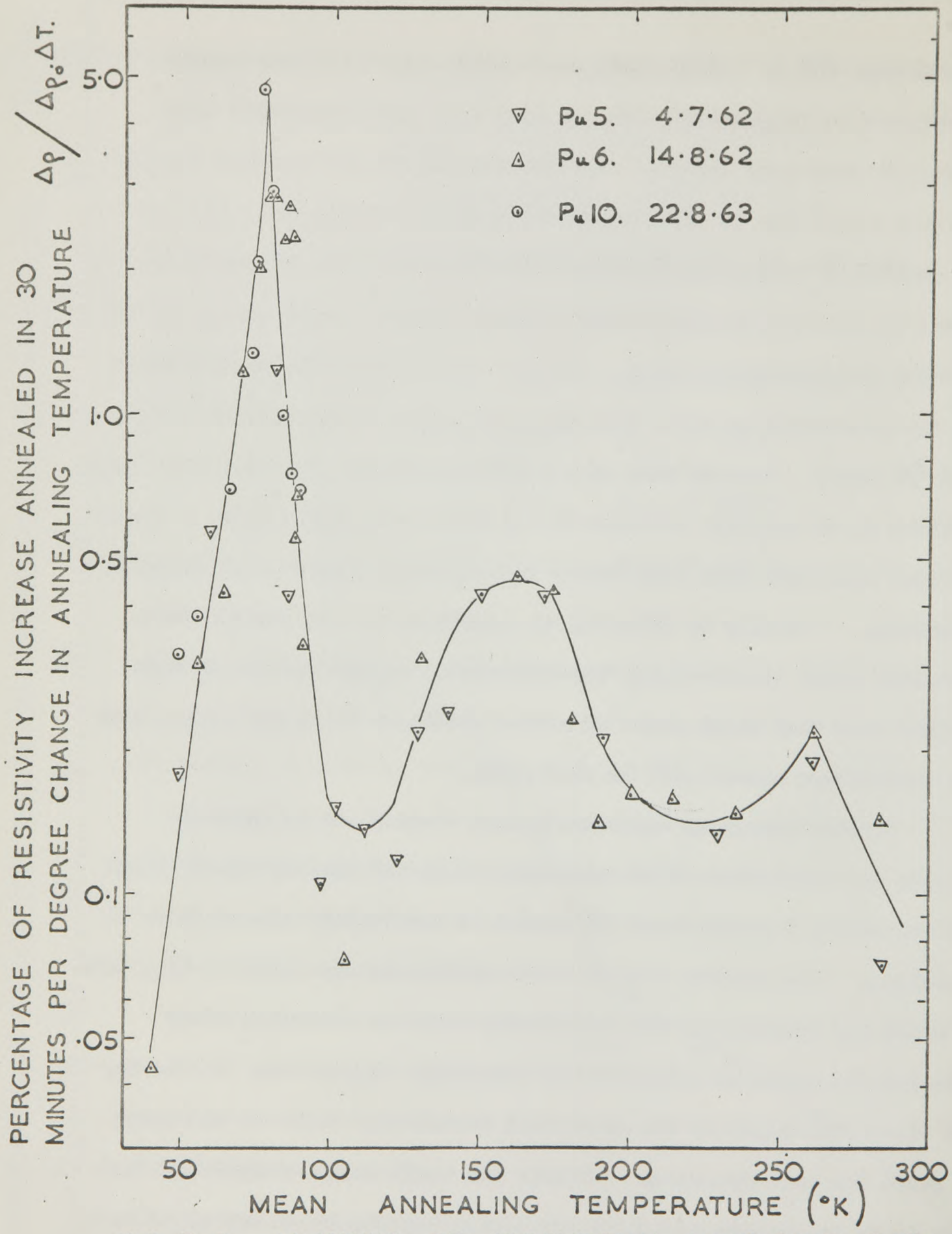


FIG. 5.3. ANALYSIS OF ISOCHRONAL ANNEALING DATA TO SHOW THE RELATIVE ANNEALING RATES OF THE DIFFERENT STAGES

poor experimental conditions with an unstable annealing temperature and the results are plotted with the limits of the temperature drift shown. Some idea of the relative efficiencies of the two main annealing stages can be obtained from the slopes of the curve in Fig. 5.2. This is also shown in Fig. 5.3. in which the percentage of the total additional resistivity, annealing in 30 minutes per degree change in the annealing temperature, $\left(\frac{\Delta\rho_{(i+1)} - \Delta\rho_i}{\Delta\rho_0 (T_{i+1} - T_i)} \right)$ is plotted as a function of the mean annealing temperature $(T_{i+1} + T_i)/2$. The results from three specimens of α plutonium are included, and are plotted with a logarithmic ordinate for convenience not because of any special significance. It can be seen that the annealing rate reaches a sharp maximum at $\sim 80^{\circ}K$ of about 4% per $^{\circ}K$ change in annealing temperature, while the broader maximum of the second stage at $\sim 160^{\circ}K$ has a value of $\sim 0.5\%$ per $^{\circ}K$ change in annealing temperature. A third annealing stage at $\sim 260^{\circ}K$ also appears in Fig. 5.3., but its validity is questionable in view of the small number of data points taken in this region.

Analysis of the rate Kinetics of the isothermal annealing experiments to be described in Chapter 6 raised doubts as to whether the first annealing stage at $\sim 80^{\circ}K$ was really composed of two sub-stages. In order to try to clarify this point a further isochronal anneal was performed on α Pu. 10 with as many data points as possible in the range ~ 40 to $\sim 90^{\circ}K$. The results of this experiment are shown in Figs. 5.4. and 5.5. In Fig. 5.4. the fraction of the additional resistivity remaining after annealing is shown as a function of annealing temperature, while in Fig. 5.5. the annealing rate $\left(\frac{\Delta\rho_{(i+1)} - \Delta\rho_i}{\Delta\rho_0 (T_{i+1} - T_i)} \right)$ is shown as a function

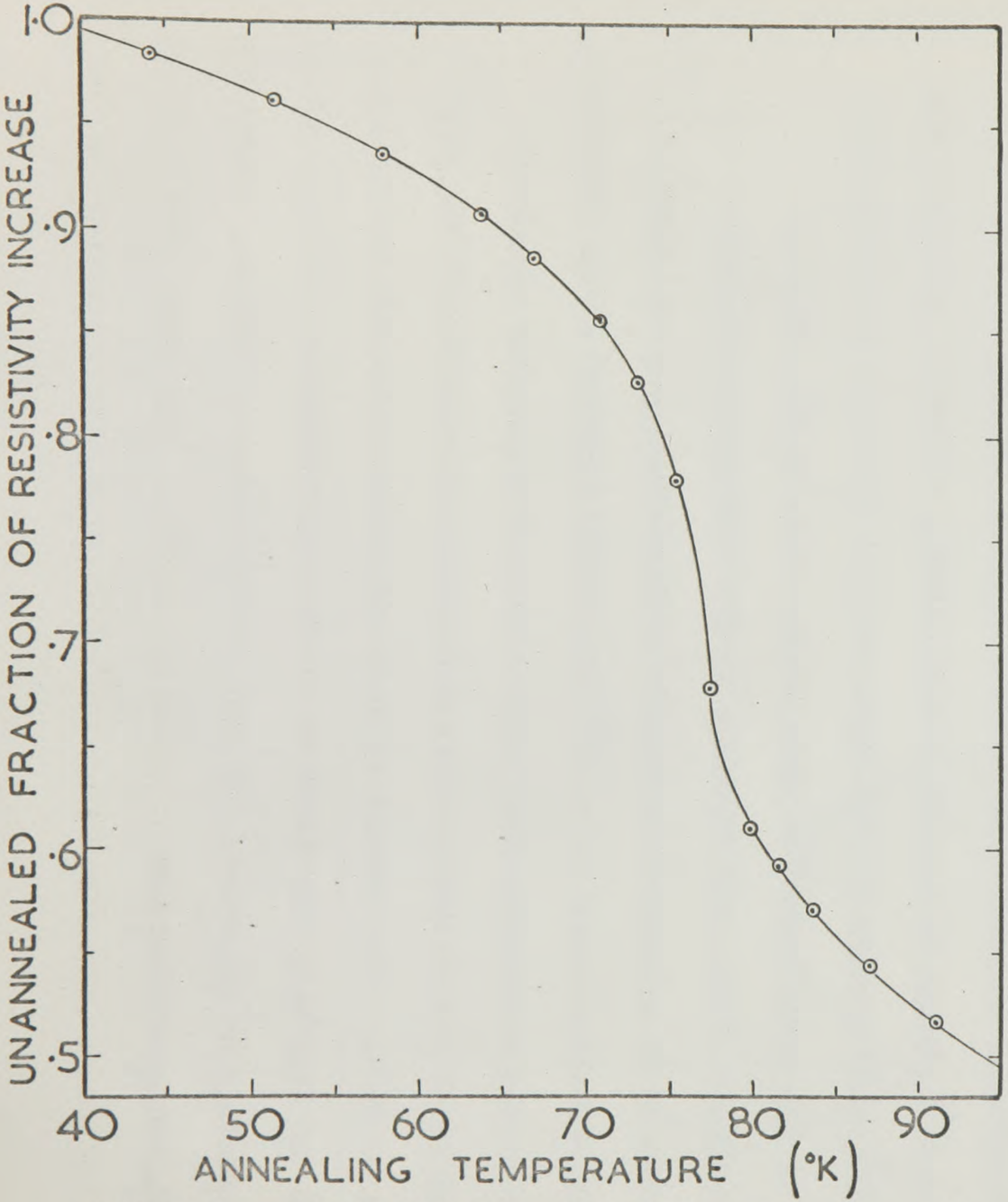


FIG. 5.4. ISOCHRONAL ANNEAL OF α Pu 10 SHOWING FIRST ANNEALING STAGE

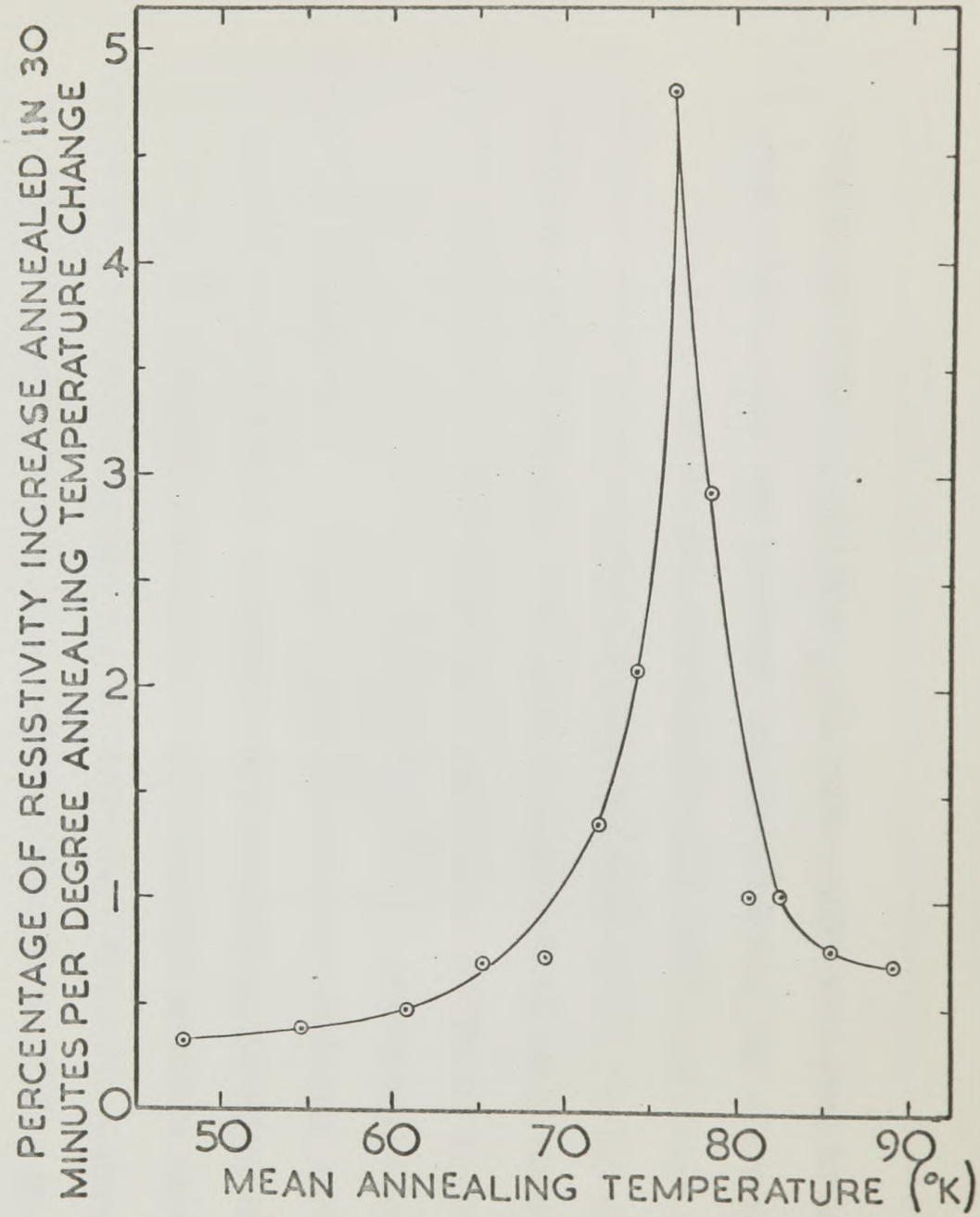


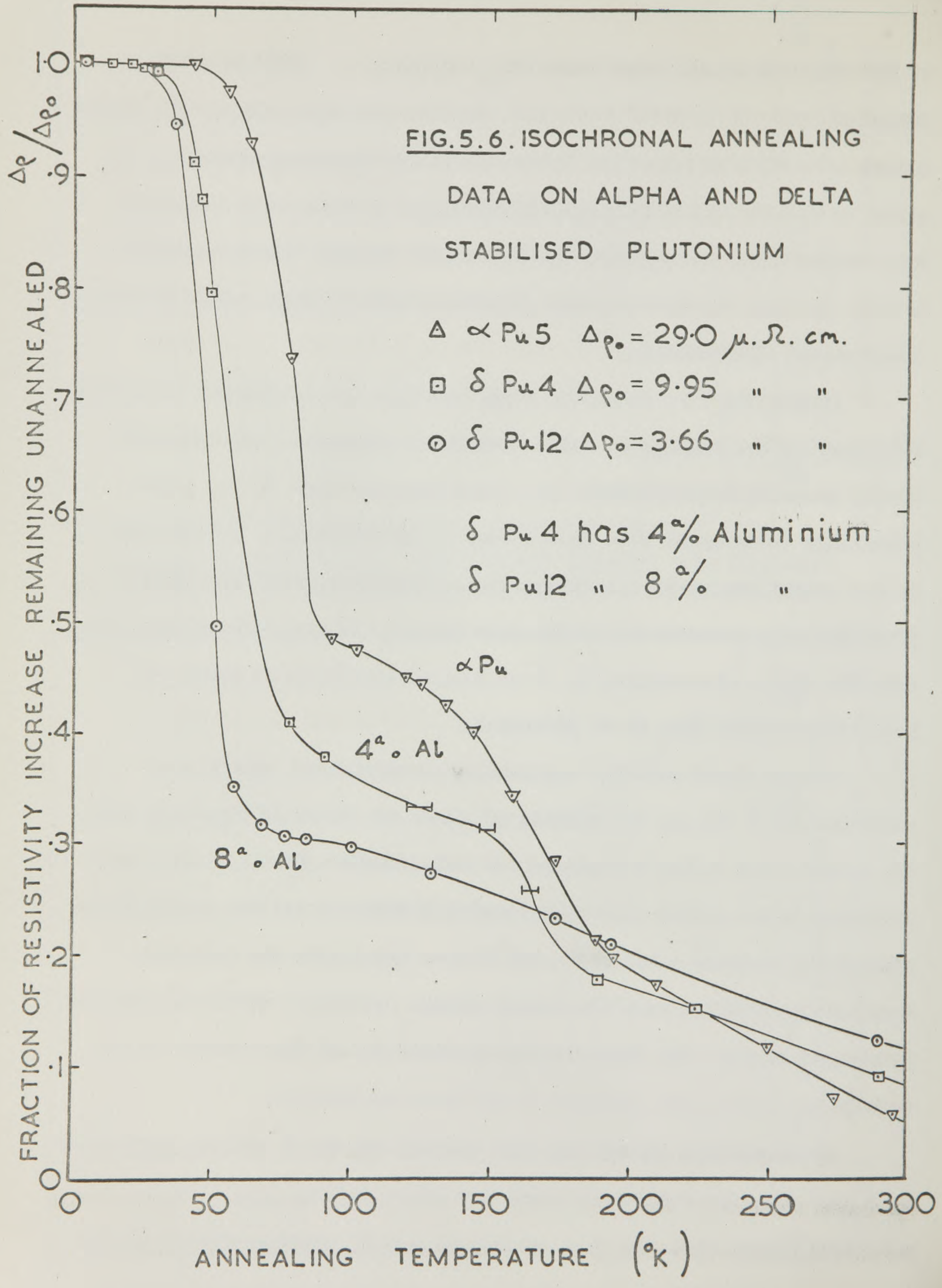
FIG. 5.5. ANALYSIS OF THE DATA OF FIG. 5.4. TO SHOW ANNEALING RATE

of the mean annealing temperature $(T_{i+1} + T_i)/2$. Neither of these diagrams shows the existence of more than one annealing stage, the slight offset at $\sim 67^{\circ}K$ in Fig. 5.5. being within the experimental error. In order to obviate the possibility of substages in this range even more data points would be required but this would involve either overnight storage or runs of about 24 hours duration, both of which would introduce experimental difficulties.

Finally in this chapter we shall consider the isochronal annealing behaviour of two samples of delta stabilised plutonium. In Fig. 4.1. it was shown that considerable annealing occurred when δ Pu. 4 was physically transferred from one storage dewar to another, in contrast to the slight degree of annealing which occurred when samples of α plutonium were transferred in the same manner. It was deduced from this that the onset of annealing in δ stabilised plutonium occurred at a lower temperature than in α plutonium.

At the first suitable opportunity an isochronal anneal was performed on δ Pu. 4, the results of which are shown in Fig. 5.6. with the result from α Pu. 5 included for comparison. The experiment was performed under rather poor experimental conditions and the measurements carried out between ~ 100 and $\sim 180^{\circ}K$ were taken with the annealing temperature drifting over the ranges shown. A further error was probably introduced because the thermocouple junction was on the outside of the capsule and not on the specimen as in later experiments.

An isochronal anneal was also carried out on δ Pu. 12, stabilised by 8 At.% Al., the results of which are shown in Fig. 5.6. The annealing period used for this experiment was 20 minutes instead of the


FIG. 5.6. ISOCHRONAL ANNEALING DATA ON ALPHA AND DELTA STABILISED PLUTONIUM
△ α Pu 5 Δρ₀ = 29·0 μ.Ω. cm.
⊡ δ Pu 4 Δρ₀ = 9·95 " "
⊙ δ Pu 12 Δρ₀ = 3·66 " "
δ Pu 4 has 4% Aluminium
δ Pu 12 " 8% "
α Pu
4% Al
8% Al
Δρ/Δρ₀
FRACTION OF RESISTIVITY INCREASE REMAINING UNANNEALED
0
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
0
50
100
150
200
250
300
ANNEALING TEMPERATURE (°K)

30 minutes used in all other annealing experiments. This shorter period was chosen in order to be able to obtainas many data points as possible in the short time available for the experiment. Strict comparisons between the annealing behaviour of the two delta samples are not possible, but certain trends are noticeable.

i) The onset of annealing occurs at an even lower temperature for the 8 At.% Al. δ specimen, $\sim 32^{\circ}K$, than for the 4 At.% Al. δ specimen, $\sim 35^{\circ}K$, and for the α specimen, $\sim 40^{\circ}K$.

ii) Almost 70% of the resistivity increase is removed by the first annealing stage in the 8 At.% Al. δ specimen, compared with $\sim$ 60% for the 4 At.% Al. δ specimen and $\sim$50% for the α specimen.

iii) The second, $\sim 160^{\circ}K$ annealing stage is almost completely absent in the 8 At.% Al. specimen, and is smaller for the 4 At.% Al. δ specimen than for the α specimen.

iv) After annealing to room temperature $\sim$ 13% of the resistivity increase in the 8 At.% Al. δ specimen remained un-annealed compared with $\sim$9% for the 4At.% Al. δ specimen and $\sim$5% for the alpha specimen.

Further comparisons between the annealing behaviour of the different compositions of δ stabilised plutonium and the α sample must be qualified by considering the differences in the initial resistivity increases and self-irradiation times of the samples. For the three specimens shown in Fig. 5.6. the relevant facts are those given in Table 5.A.

No annealing rate diagram is given for the delta stabilised specimens because of the relatively few data points obtained. Comparisons between the annealing behaviour of specimens with different initial

defect concentrations or with a greater range of aluminium contents was not possible before experimental work ceased.

TABLE 5.A.

Sample	Composition	Irradiation time at 5°K (hours)	Additional Resistivity ($\mu\Omega$cm.)
Pu. 4	4 At.% Al.	920	9.95
Pu. 12	8 At.% Al.	665	3.66
Pu. 5	-	640	29.00

We are extremely reluctant even to speculate on the possible nature of the defects which are annealed in the stages described above, especially as there is by no means complete agreement among the various workers in this field on the types of defects annealed in simple metals such as copper. In table 5.B. we give the results obtained by Corbett, Smith and Walker (1959 a and b) for electron irradiated copper.

TABLE 5.B.

Annealing stages in electron-irradiated copper

Annealing Stage	Temperature (°K)	Order of Reaction	Type of Defect involved
I A,B & C	14-33	1st	Recombination of close i-v pairs
I D	33 - 48	2nd	Free diffusion of correlated interstitials
I E	48 - 65	2nd	" " of un-correlated interstitials
II	65 - 233	1st	Release of interstitials from traps
III	233 - 373	2nd	Migration of di-interstitials
IV	373 - 473	-	Migration of vacancies
V	473	-	Recrystallisation
Melting Point	1356		

Thompson (1960) prefers to attribute stage III to the migration of vacancies, with recrystallisation occurring in stage IV and no stage V. Furthermore he states that as a general rule stage III occurs at 0.2 T_m and with an activation energy $E = 5 \times 10^{-4} T_m$ eV where T_m °K is the melting point of the metal concerned. For plutonium $T_m \sim 910$°K hence 0.2 $T_m \simeq 180$°K and E = 0.45 eV. This is approximately the temperature of our second annealing stage. Unfortunately we have neither measured its activation energy nor annealing Kinetics. Although there is not a well defined relationship between stage I annealing and T_m it is usually found that stage I annealing is complete by 0.5 T_m, which for plutonium would be ~ 45°K. For the δ specimens our first annealing stage occurs at a slightly higher temperature, while for α plutonium the ~ 80°K stage is more nearly at 0.1 T_m. Furthermore we have shown that at ~ 90°K second order Kinetics are obeyed during the anneal, which would apparently rule out its identification with stage II. Thus the nearest we can get to identifying the first annealing stage of α plutonium is to say that it is just possible that at ~ 90°K we have stage I_D and I_E recovery and that earlier stages have been missed or are absent.

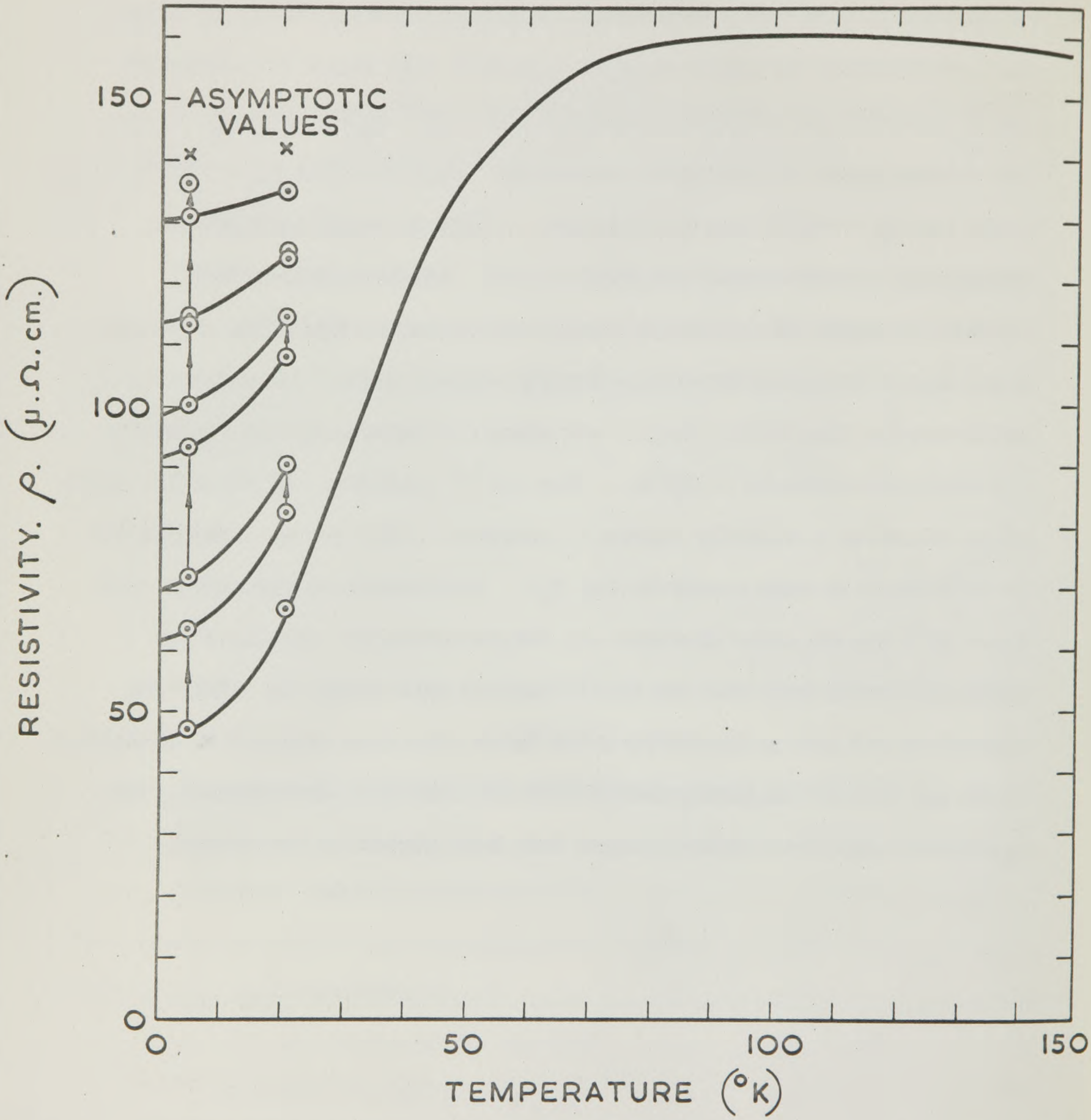


FIG.6.1 RESISTIVITY vs TEMPERATURE CURVES FOR Pu 2 IN THE UNDAMAGED AND DAMAGED STATES DURING HOLDING IN LIQUID HELIUM AND HYDROGEN.

CHAPTER 6*

Isothermal Annealing Studies of Heavily Damaged Alpha Plutonium

6.1. Experimental Results

In Chapter 3 we described how the highly temperature dependent low temperature resistivity of sample α Pu. 2 became, under the influence of self-irradiation damage, less and less temperature dependent as it accumulated more defects. This was shown in Fig. 3.4 which we repeat now as Fig. 6.1. It can be seen that after 5,000 hours below $\sim 20^{\circ}K$ the $\sim 5^{\circ}K$ resistivity rose from $\sim 47\ \mu\Omega$ cm. to $\sim 136\ \mu\Omega$ cm. and was tending towards an asymptotic value of $\sim 141\ \mu\Omega$ cm. Similarly the $\sim 20^{\circ}K$ resistivity rose from $\sim 57\ \mu\Omega$ cm. towards an asymptotic value of $\sim 141 - 142\ \mu\Omega$ cm. After 4,952 hours below $\sim 20^{\circ}K$ the $\sim 5^{\circ}K$ resistivity was measured as $136.33\ \mu\Omega$ cm. and an attempt was made to record the $\sim 20^{\circ}K$ resistivity by transferring the specimen to a bath of liquid hydrogen. Unfortunately the German silver tube surrounding the leads fractured during this transfer and the specimen had to be removed to a bath of liquid nitrogen while repairs were effected. After 19 hours spent in liquid nitrogen the resistivity measured at $\sim 77^{\circ}K$ was found to be $147.7_0\ \mu\Omega$ cm, over 11 $\mu\Omega$ cm. lower than its original undamaged

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*Part of the subject matter of this chapter has been published in papers by Lee, J.A., Mendelssohn, K., and Wigley, D.A. Conf. Lattice Defects, Kyoto, 1962, to be published, and Cryogenics 3, 46, (1963).

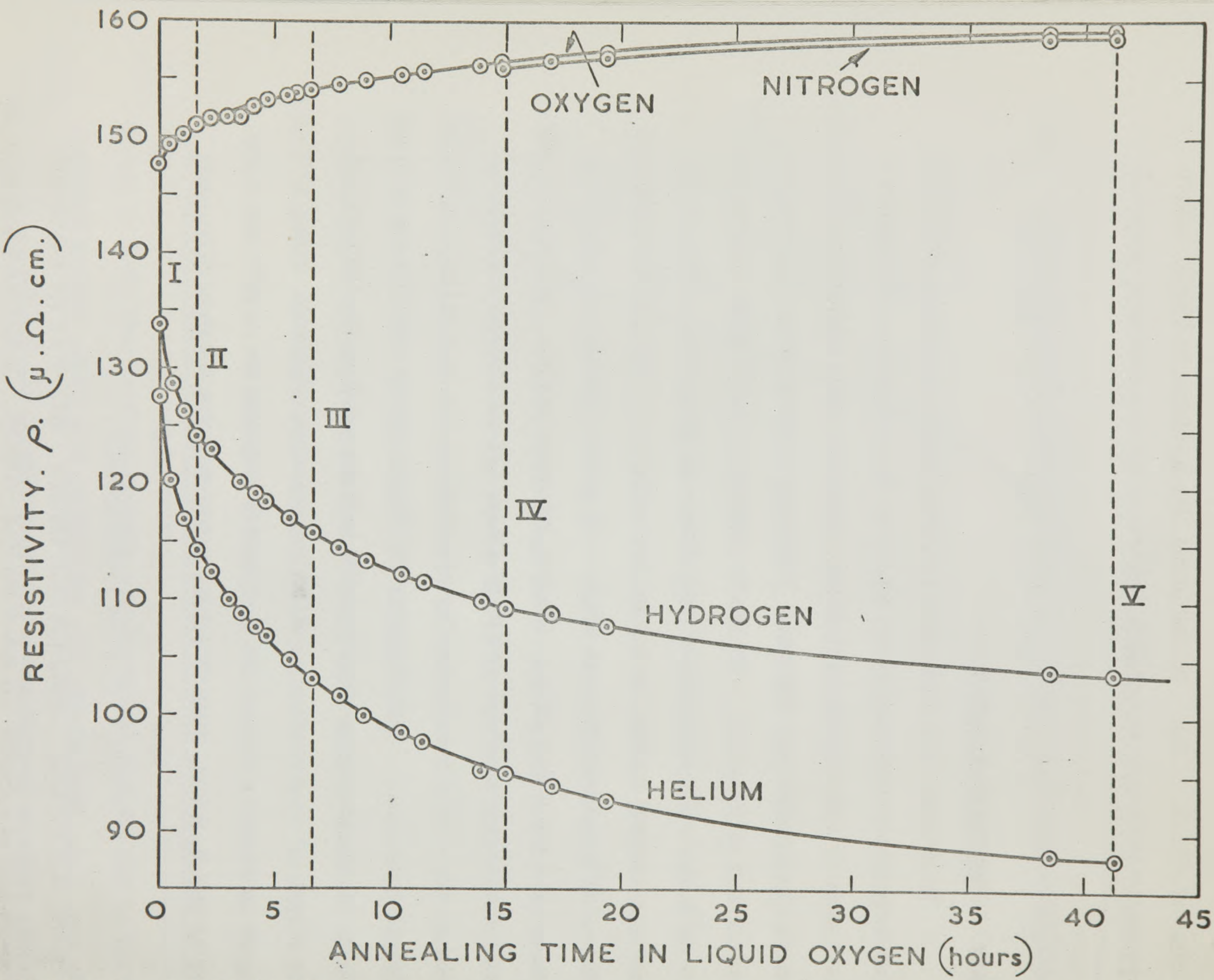


FIG. 6.2. ISOTHERMAL ANNEAL OF Pu 2 AFTER 5000 HOURS IN LIQUID HELIUM.

value of 158.94 $\mu\Omega$ cm. On returning the specimen to liquid helium the resistivity was found to be 127.62 $\mu\Omega$ cm. showing that some annealing had taken place during the time spent in liquid nitrogen. Transfer of the specimen to a bath of liquid hydrogen showed the ~ 20°K resistivity to be 133.73 $\mu\Omega$ cm.

These were the various resistivity values at the beginning of an isothermal anneal performed on α Pu. 2 at ~ 90°K. The specimen was transferred from the liquid helium dewar into a bath of liquid oxygen and held there for about 30 minutes and its resistivity measured at ~ 90°K a few times during this period. It was then transferred to liquid nitrogen and its ~ 77°K resistivity was determined. Subsequently it was returned to the helium dewar and its ~ 5°K resistivity was measured before transfer to a bath of liquid hydrogen where its ~ 20°K resistivity was measured. The specimen was then returned to the bath of liquid oxygen and the cycle of anneal and measurement was repeated. The specimen was moved from liquid nitrogen to liquid helium and then to liquid hydrogen in order to minimise the amount of hydrogen gas evolved into the laboratory as very great care was needed in handling liquid hydrogen in a laboratory which could not be vented to the atmosphere by opening windows. The results obtained from this experiment are shown first in Fig. 6.2. where the resistivities measured at ~ 5°, ~20°, ~ 77° and ~ 90°K are shown as a function of the time spent by the specimen annealing at ~ 90°K. The following features may be noted:

a) The resistivities measured at ~77 and ~ 90°K rose as the anneal proceeded, eventually reaching the values that they had on first cooling in the undamaged state.

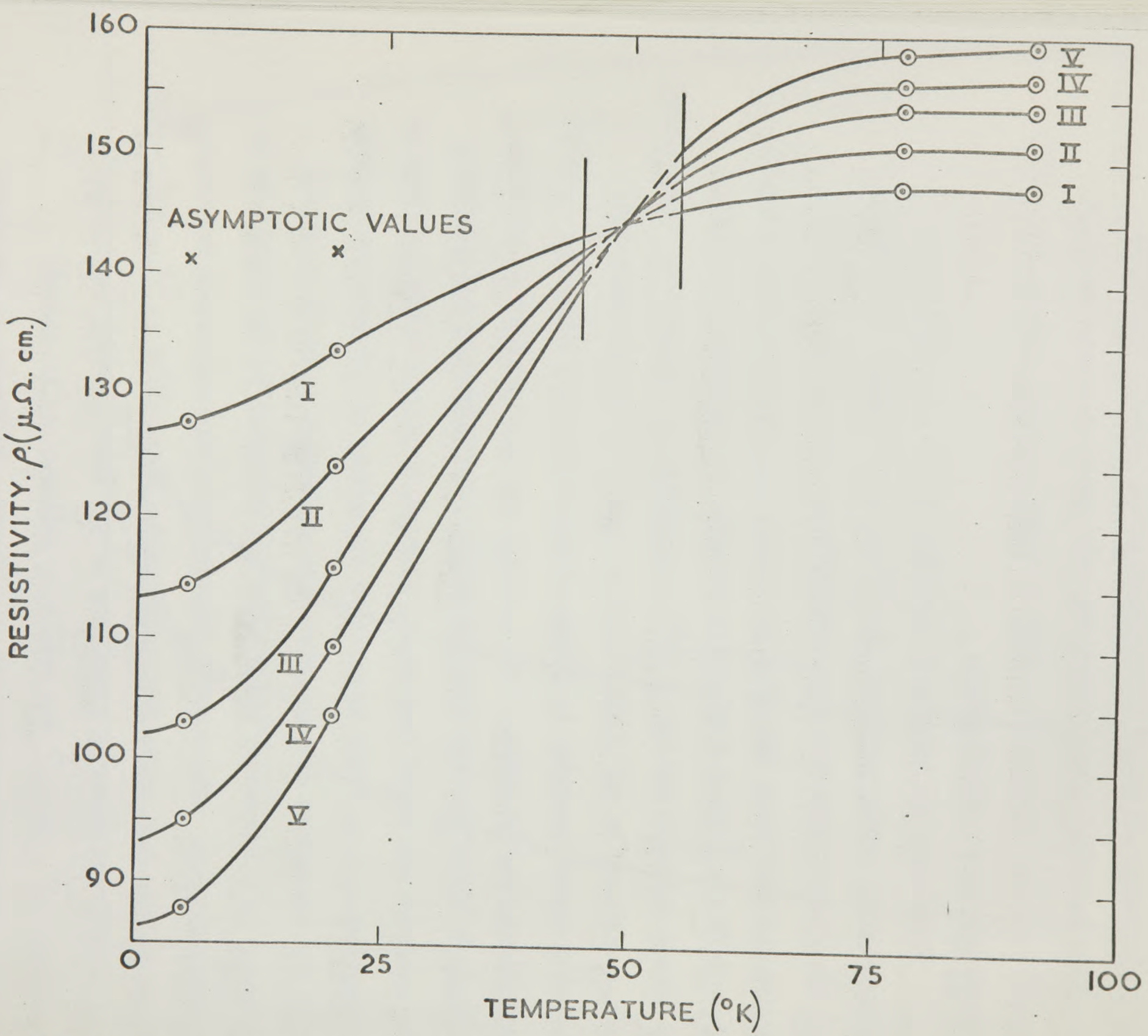


FIG. 6.3. RESISTIVITY vs TEMPERATURE CURVES AT DIFFERENT STAGES OF ANNEAL AT 90°K OF Pu2.

b) The resistivities measured at ~ 5°and ~20°K fell as the anneal proceeded, eventually reaching values of ~ 87.3 μΩcm. and 103.6 μΩcm. respectively. These values represent a drop to about 46% of the total resistivity increase which is in very good agreement with the data shown in Fig. 5.2. for the first stage in the isochronal annealing spectrum of α plutonium.

c) The difference in resistivity at ~ 5°K and ~ 20°K, $\Delta\rho_{5-20}$ increased from ~ 6.1 μΩcm. at the beginning of the anneal to ~ 16.0 μΩcm. at the end of the anneal, which was still not equal to the original value of 19.8 μΩ cm. on first cooling. Evidently the defects not removed during the liquid oxygen anneal still affect the ~ 5 and ~ 20°K resistivities but not appreciably those at ~ 77 and ~ 90°K.

It will be seen from Fig. 6.2 that a series of isochronals are labelled I to V corresponding to 0, 1.5, 6.5, 15 and 41.5 hours annealing at ~ 90°K respectively. These measured values of the resistivity at ~ 5, ~ 20, ~ 77 and ~ 90°K have been used to plot the instantaneous resistivity vs. temperature curves at different stages of the anneal and are shown in Fig. 6.3. The numerals labelling these curves correspond to those labelling the isochronals in Fig. 6.2. As each curve only contains four measured points it is obvious that at best these curves are essentially free hand extrapolations of the measured data. However we believe that they are substantially correct in their form but in view of this uncertainty we would not dogmatically assert that all the curves cross at ~ 50°K but that they probably cross somewhere in the range 45 - 55°K. Below this temperature range self-irradiation damage produces an increase in the measured resistivity while above it the effect

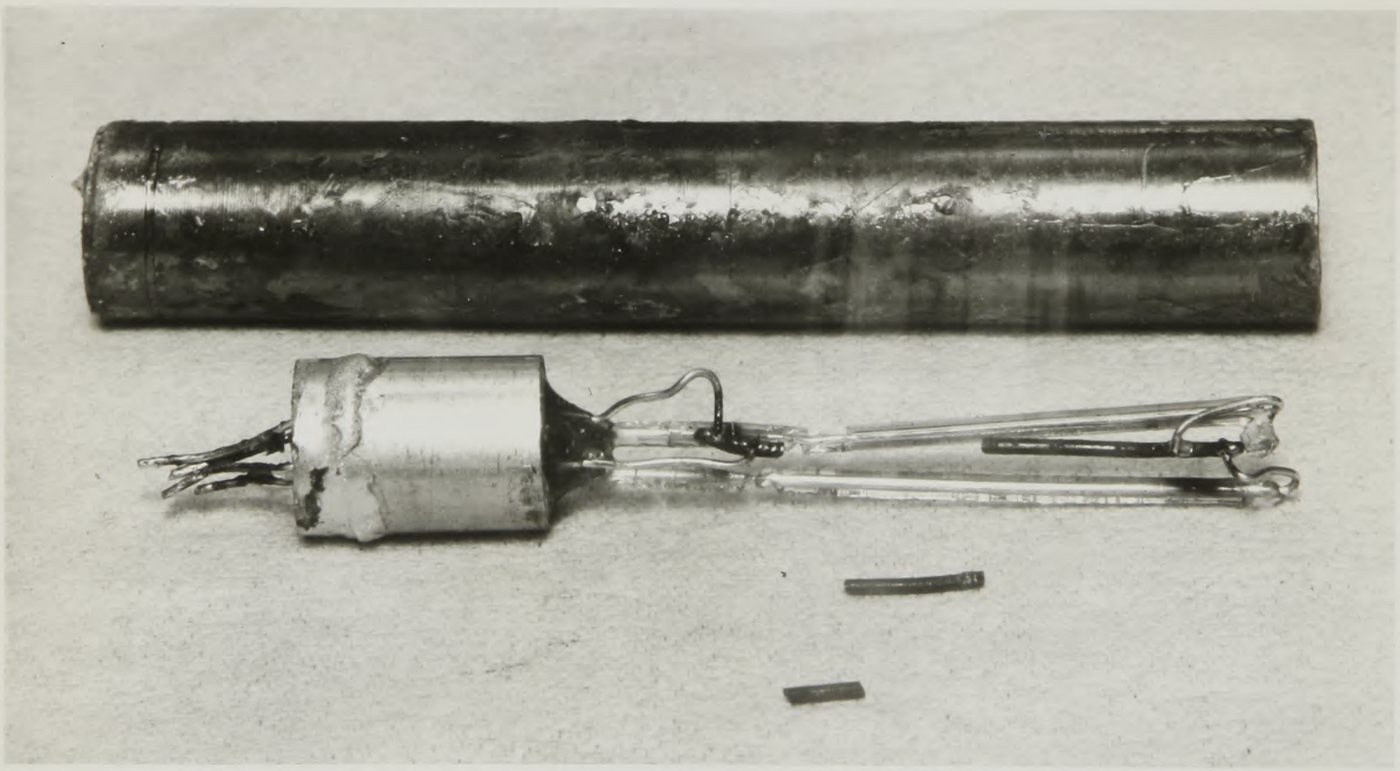


FIG. 6.4.

of the self damage built in at low temperatures is to reduce the measured resistivity. The net effect is to render the resistivity of a heavily damaged sample of α plutonium almost temperature independent at a value of $\sim 144\ \mu\Omega$ cm.

Further work was prevented by the breakage of the specimen, a photograph of which is shown demounted in Fig. 6.4. It can be seen that the specimen broke cleanly into four pieces and that there was no sign of any bending or deformation. The diameters of the specimen measured after demounting were, to within experimental error, the same as those measured before encapsulation.

In view of the rather unexpected nature of these annealing results a second sample, α Pu. 7, was encapsulated, cooled to $\sim 5^{\circ}$K and held for almost 2,000 hours. This specimen was of a lower purity than α Pu. 2 and also had a higher self heat, 2.81 mW/gm. compared with 2.04 mW/gm. for α Pu. 2. Thus the initial amounts of self damage stored in the two specimens were not the same but were similar enough to allow comparison to be made between them. The experiment was performed basically as described for that of α Pu. 2 and the results are shown in Fig. 6.5. The anneal was first carried out at $\sim 77^{\circ}$K in liquid nitrogen with periodic measurements at ~ 5, ~ 20, and $\sim 77^{\circ}$K, then after about 47 hours annealing in liquid nitrogen the annealing temperature was changed to $\sim 90^{\circ}$K and annealing proceeded in liquid oxygen with measuremonts at ~ 5, ~ 20, ~ 77 and $\sim 90^{\circ}$K. After 46 hours annealing in liquid oxygen the specimen was returned to liquid helium for 238 hours, not minutes as indicated in Fig. 6.5., and the rate of resistivity increase compared to that originally recorded for the same values of resistivity.

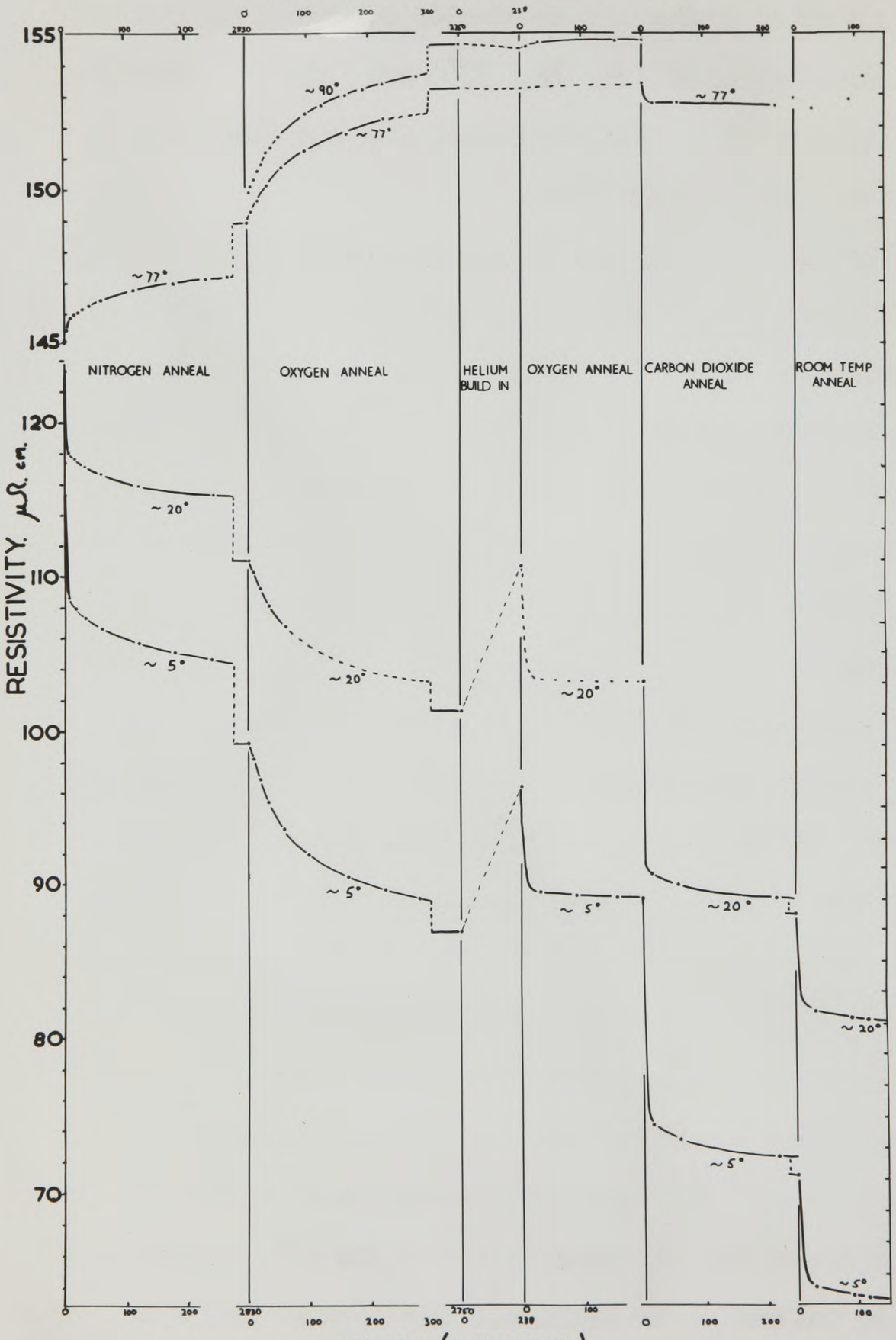

ISOTHERMAL ANNEAL OF Pu7.
RESISTIVITY. μΩ. cm.
155
150
145
120
110
100
90
80
70
NITROGEN ANNEAL
OXYGEN ANNEAL
HELIUM BUILD IN
OXYGEN ANNEAL
CARBON DIOXIDE ANNEAL
ROOM TEMP ANNEAL
~ 90°
~ 77°
~ 77°
~ 77°
~ 20°
~ 20°
~ 20°
~ 20°
~ 5°
~ 5°
~ 5°
~ 5°
~ 20°
~ 20°
~ 5°
~ 5°
TIME. (MINUTES.)

FIG. 6.5.

After brief re-annealing in liquid oxygen the specimen was further annealed in a bath of crushed carbon dioxide and methyl alcohol with resistivity measurements at ~ 5, ~ 20, ~77°K and ~195°K. Finally the specimen was warmed to room temperature with the usual periodic measurements at ~ 5, ~20 and ~77°K.

In order to include as much information as possible in Fig. 6.5. only the initial results of each anneal are shown in detail. The values of the resistivities at the end of each separate annealing stage are also shown. The results from this anneal of α Pu. 7 confirm the basic pattern shown by the anneal of α Pu. 2; that as the anneal proceeds the resistivities measured at ~ 77 and ~ 90°K increase while those measured at ~ 20°K and ~ 5°K decrease. A few points of detail arising from the anneal of α Pu. 7 are:

a) The liquid nitrogen anneal commenced extremely rapidly; the ~ 5°K resistivity dropping from 117.40 $\mu\Omega$ cm. to 108.62 $\mu\Omega$ cm. during the first $6\frac{1}{2}$ minutes at ~ 77°K. In contrast a further 28 hours at ~ 77°K were required for the ~ 5°K resistivity to drop to 99.23 $\mu\Omega$ cm. This point will be discussed further when we deal with the reaction Kinetics of this anneal.

b) At the end of the ~ 90°K anneal the resistivities at ~ 77 and ~ 90°K were slightly higher than their original undamaged values; 154.64 compared to 153.59 at ~ 90°K and 153.27 to 151.05 at 77°K. We would not put much emphasis on the subsequent values of the 77°K resistivity except to say that at the end of the experiment the value of 153.72 was about 2.7 $\mu\Omega$ cm. higher than its original value. Table 6.A. shows the comparative value of resistivity on first cooling the undamaged specimen and after

fully annealing the damaged specimen to room temperature.

TABLE 6.A.

State	Resistivity at: 293°K	90°K	77°K	20°K	5°K
Undamaged	144.91	153.59	151.05	74.69	56.56
After annealing	146.05	154.78	153.72	81.40	63.55

c) The carbon dioxide and room temperature annealing stages show an extremely rapid initial decrease in the ~ 5 and ~ 20°K resistivities but a less well defined relationship is seen in the ~ 77°K value.

d) After completion of the 90°K anneal the specimen was returned to liquid helium for ~ 238 hours during which time its resistivity rose from ~ 86.9 to 96.36 $\mu\Omega$ cm. at an average rate of .0396 $\mu\Omega$ cm/hr. During the original self damage period in liquid helium the average rate of resistance increase over the range ~ 87 to ~ 96 $\mu\Omega$cm. was .0329 $\mu\Omega$ cm. Thus after annealing most of the defects mobile at ~ 90°K, re-storage of these defects proceeded at a slightly faster rate than during the original damage period at ~ 5°K.

Having found from the results on α Fe. 2 that long periods of self-irradiation damage at low temperatures rendered the resistivity below ~90°K almost temperature independent we thought that it would be of considerable interest to see to what temperatures this temperature independent behaviour existed. As it was known that strong annealing occurred from ~ 80°K upwards we decided to warm a heavily damaged specimen as quickly as possible to ~250°K taking measurements at convenient

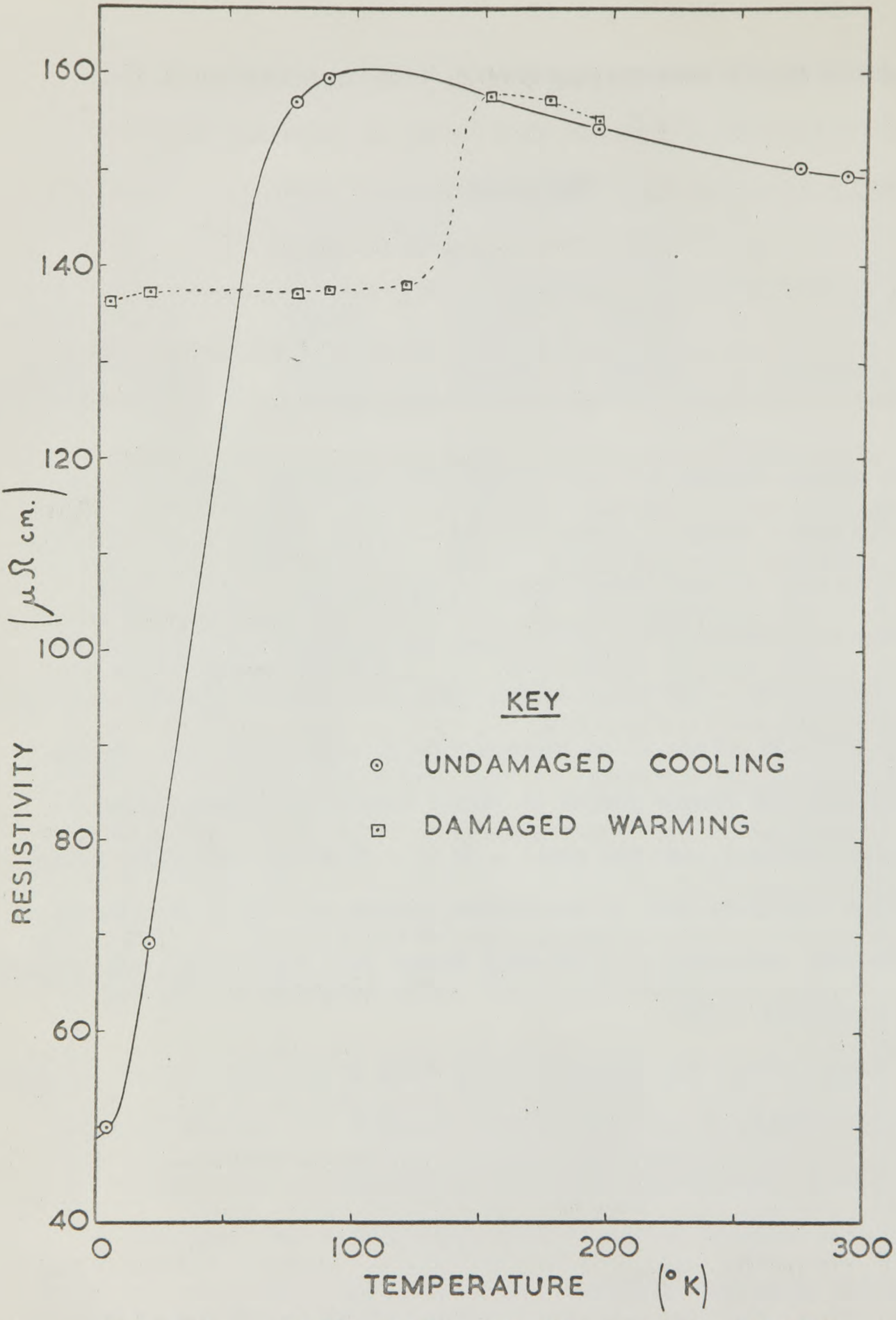


FIG. 6.6. FAST WARM UP OF ∝Pu.6. AFTER 8,200 HOURS AT 5°K

temperatures during this warming period. The specimen would then be quenched back to ~5°K to see what degree of annealing had taken place during this warm up. The experiment was performed on specimen α Pu. 6 after almost 8,200 hours self-irradiation at ~5°K. The results of this experiment are shown in Fig. 6.6. in which the resistivities measured on first cooling are shown together with those taken during the rapid warm up of the damaged specimen. It can be seen that the resistivity of the damaged specimen remained almost independent of temperature at ~ 138 $\mu\Omega$ cm. from ~5 to ~120°K. There was then a sudden increase between ~120 and ~152°K to a value of ~ 157.5 $\mu\Omega$ cm, which was very slightly higher than its original value in the undamaged state. Further warming caused the resistivity to decrease slowly with virtually the same temperature dependence as in the undamaged state, although at a slightly higher resistivity. No measurements were obtained at temperatures higher than ~195°K because of an experimental failure.

The most probable interpretation of these results is that strong annealing occurred between ~120 and ~150°K; reference to Fig. 5.3. will show that the second annealing stage has its maximum efficiency at ~150 to ~160°K. It is perhaps surprising that there was no sign of first stage annealing during warming of the damaged specimen. Confirmation of this hypothesis would have been obtained if, after warming to ~ 200°K the specimen had been quenched back to ~ 5°K. If the ~5°K value was then much lower than its pre-anneal value, and if on subsequent re-warming the resistivity vs. temperature curve had essentially the same shape as for the undamaged specimen, the explanation of rapid annealing between

~ 120 and $\sim 150^{\circ}K$ would have been confirmed. No experiment of this type was however performed because of the experimental failure already mentioned.

6.2. Determination of the Reaction Kinetics of the $\sim 80^{\circ}K$ annealing stage

It is often found that c, the number of defects of a particular kind present at time t obeys the differential equation of the form

$$-dc/dt = K f(c) \qquad 6.i.$$

where f(c) is some function of c and K is the rate constant usually with a Boltzman temperature dependence $K = K_0 e^{-E/KT}$ 6.ii. T is the absolute temperature and E is the activation energy of the particular reaction considered.

If $f(c) = c^n$ 6.iii.

the reaction is said to be of order n and we have

$$-dc/dt = K c^n \qquad 6.iv.$$

The simplest type of reaction is one of first order, i.e. a monomolecular process with $n = 1$

then $-dc/dt = K c$ 6.v.

Integrating $c = KB e^{-t}$

now at $t = o \quad c = c_o$ thus $B = c_o$

hence $c = c_o K e^{-t}$ 6.vi.

If some physical property such as the resistivity change associated with

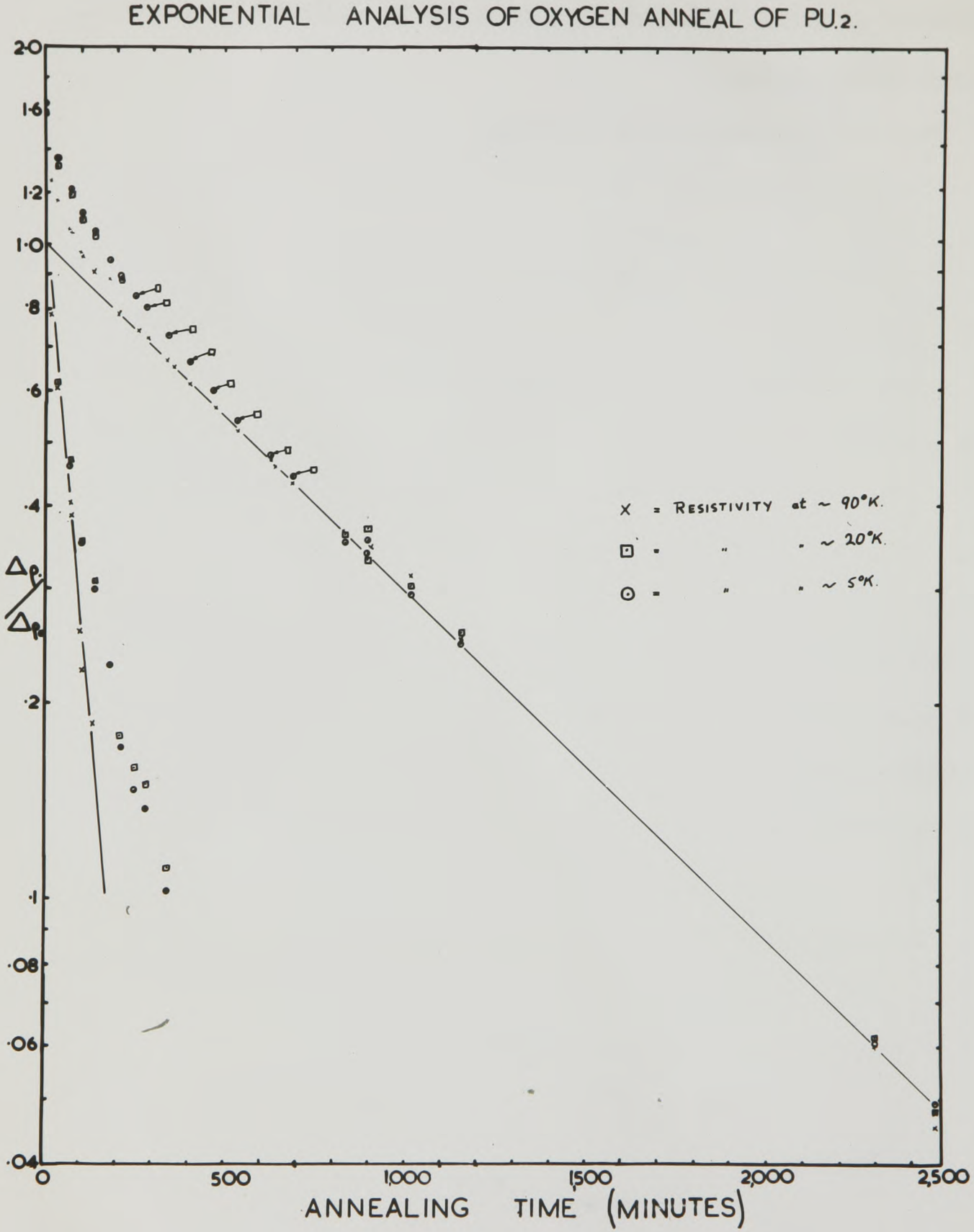

EXPONENTIAL ANALYSIS OF OXYGEN ANNEAL OF PU.2.
2·0
1·6
1·2
1·0
·8
·6
·4
·2
·1
·08
·06
·04
Δρ / Δρ₀
0
500
1,000
1,500
2,000
2,500
ANNEALING TIME (MINUTES)
× = RESISTIVITY at ~ 90°K.
⊡ = " " ~ 20°K.
⊙ = " " ~ 5°K.

FIG. 6.7.

the type of defect considered, $\Delta\rho$, is a single valued function of c independent of t and T, then changes in c may be followed by measuring the resistivity change $\Delta\rho$.

Then for a monomolecular recovery

$$\log \frac{\Delta\rho}{\Delta\rho_o} \propto t \qquad \text{6.vii}$$

Our initial analysis of the results of the isothermal anneal of α Pu. 2 at $\sim 90^{\circ}K$ seemed to show that the resistivity change during this anneal could be analysed by assuming that it consisted of the super-position of two such monomolecular recoveries, one having a much shorter time constant than the other. This analysis is shown in Fig. 6.7 and was reported briefly by Lee, Mendelssohn and Wigley (1963 a) and (1963 b). At the time this seemed a reasonable analysis and the component of small time constant was taken to indicate that there was a lower temperature annealing stage still partially unannealed. However after carefully searching for this sub-stage without success, see Fig. 5.4. and 5.5., we decided to re-analyse the annealing data of α Pu. 2 and also that of α Pu. 7 in terms of a higher order recovery process.

Returning now to equation 6.iv. we had

$$-dc/dt = K c^n \qquad \text{6.iv.}$$

separating the variables we have

$$-Kdt = c^{-n}dc \qquad \text{6.viii}$$

integrating

$$-Kt + \alpha = \frac{1}{-n+1} c^{-n+1}$$

Now if at $t = o \quad c = c_o$

$$\alpha = \frac{1}{-n+1} c_o^{-n+1}$$

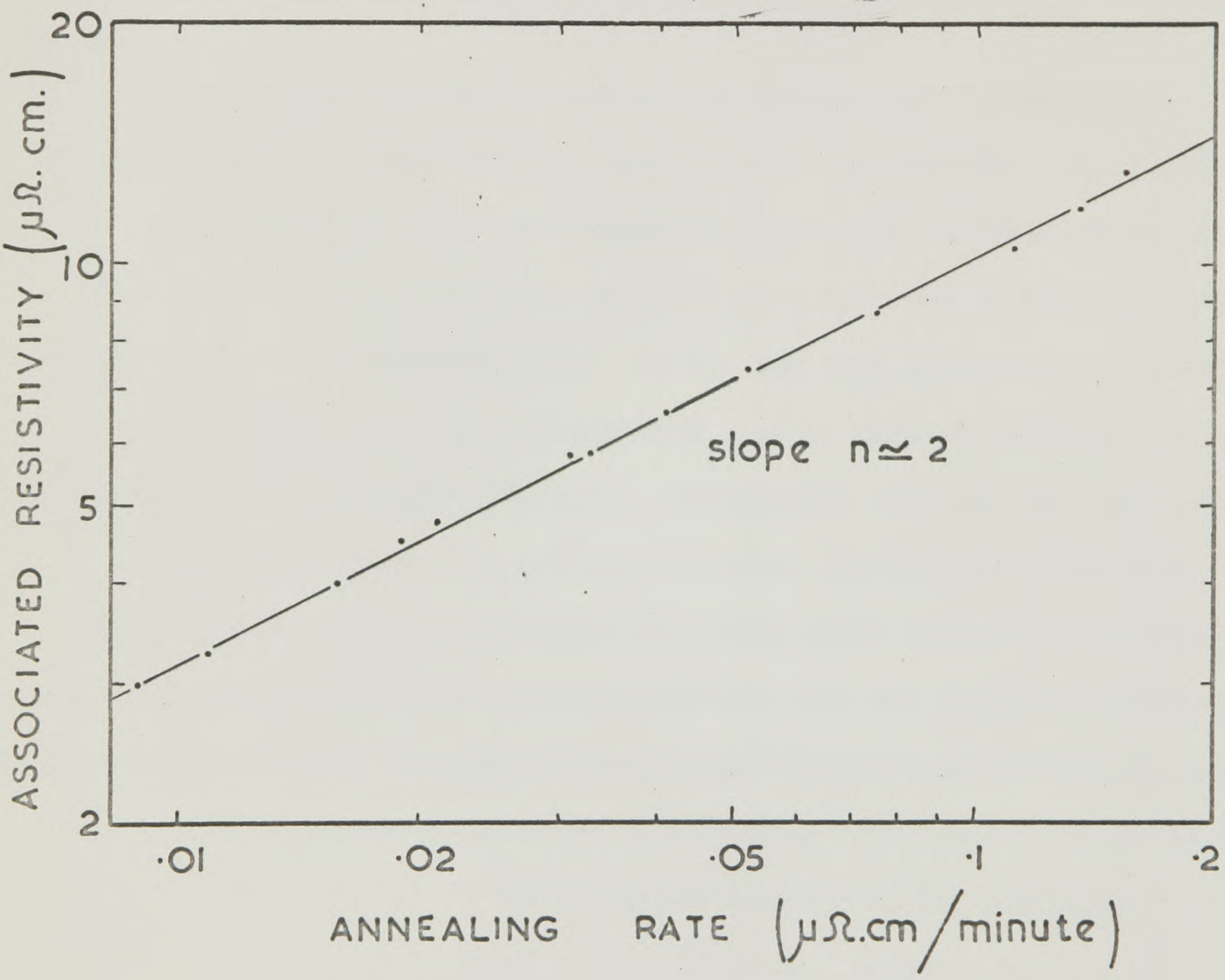
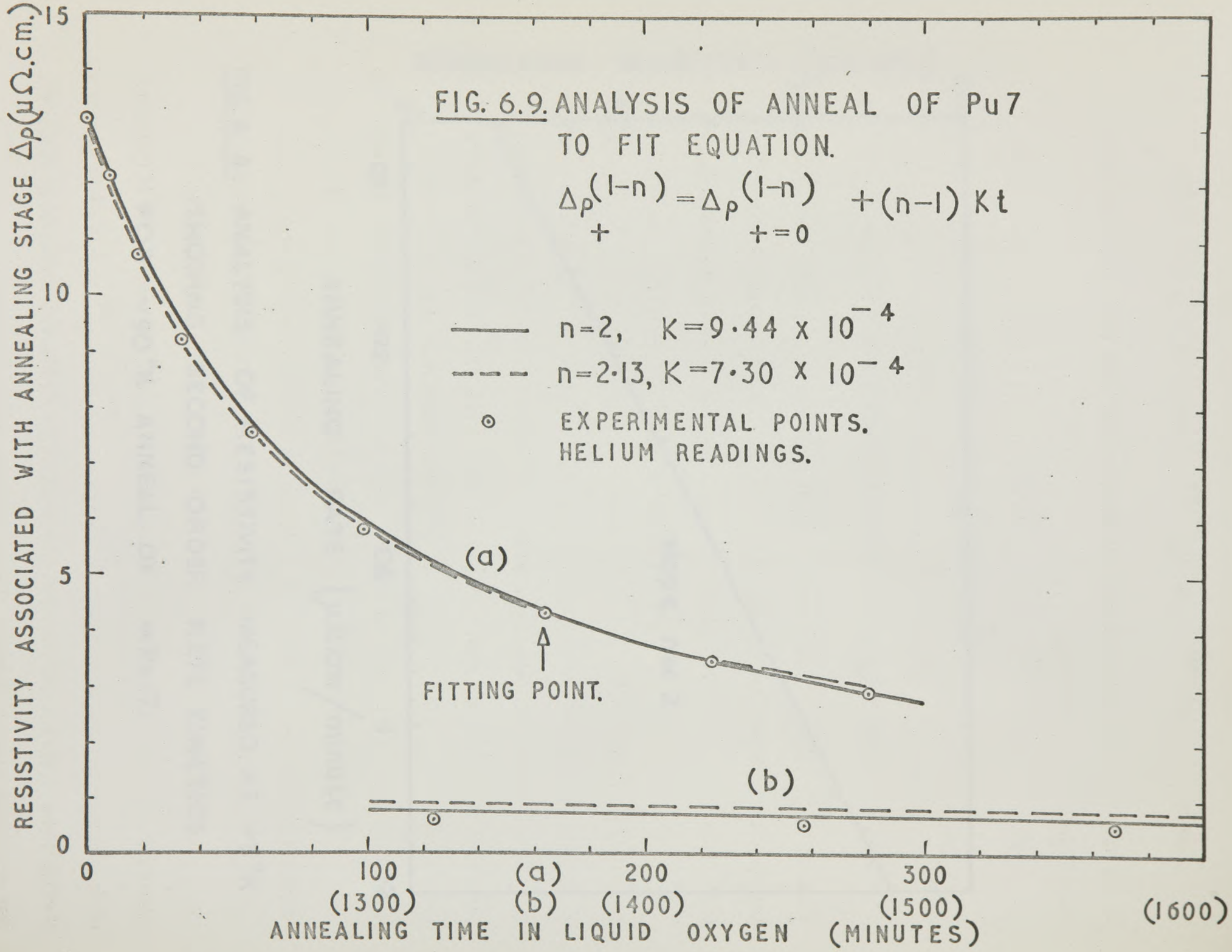


FIG. 6. 8. ANALYSIS OF RESISTIVITY MEASURED AT ~5°K SHOWING SECOND ORDER RATE KINETICS FOR ~90°K ANNEAL OF ∝Pu. 7.


FIG. 6.9. ANALYSIS OF ANNEAL OF Pu7 TO FIT EQUATION.
$\Delta\rho_{+}^{(1-n)} = \Delta\rho_{+=0}^{(1-n)} + (n-1)\,Kt$
n=2, K=9·44 x 10⁻⁴
n=2·13, K=7·30 x 10⁻⁴
EXPERIMENTAL POINTS. HELIUM READINGS.
(a)
(b)
FITTING POINT.
RESISTIVITY ASSOCIATED WITH ANNEALING STAGE Δρ(μΩ.cm.)
15
10
5
0
0
100
(1300)
(a)
(b)
200
(1400)
300
(1500)
(1600)
ANNEALING TIME IN LIQUID OXYGEN (MINUTES)

hence $c^{(1-n)} = c_o^{(1-n)} + (n-1)\,Kt$ ——— 6.ix.

If as before c is proportional to the resistivity increase associated with this annealing stage $\Delta\rho$,

then $\Delta\rho^{(1-n)} = \Delta\rho_o^{(1-n)} + (n-1)\,Kt$ ——— 6.x.

Also $-\frac{d\Delta\rho}{dt} = K\,\Delta\rho^n$ ——— 6.xi

and $\log -\frac{d\Delta\rho}{dt} = \log K + n \log \Delta\rho$ ——— 6.xii.

Thus if $-\frac{d\Delta\rho}{dt}$ and $\Delta\rho$ are measured for a particular anneal and plotted on log-log co-ordinate paper the slope of the linear relationship between them will have a value n if the anneal obeys n^{th} order reaction Kinetics.

This was done for the ~ 5°K resistivity measured during the oxygen anneal of α Fig. 7 and the resultant graph is shown in Fig. 6.8. It can be seen that the slope has a value between n = 2.0 and n = 2.1_3. The curves shown in Fig. 6.9. were constructed from the values obtained by substituting n = 2.1_3 and n = 2.0 in Eqn. 6.x. and fitting the measured values of $\Delta\rho_{t=0}$ and $\Delta\rho_{t=160}$ to find the values of the coefficient K. The value of n = 2.0 can be seen to give a better general fit than n = 2.1_3.

It would appear then that to within experimental error the ~ 5°K resistivity values measured as a function of time annealed in liquid oxygen, obey second order reaction Kinetics. To check this further the normalised resistivity values $\frac{\Delta\rho}{\Delta\rho_o}$ for the ~5°, ~20°, ~77° and ~90°K readings were plotted as a function of annealing time at ~ 90°K together with a curve of the 2nd order function $\Delta\rho^{-1} = \Delta\rho_o^{-1} + K\,t$ also suitably normalised. These curves are shown in Fig. 6.10. demonstrating that all the measured values closely follow second order Kinetics.

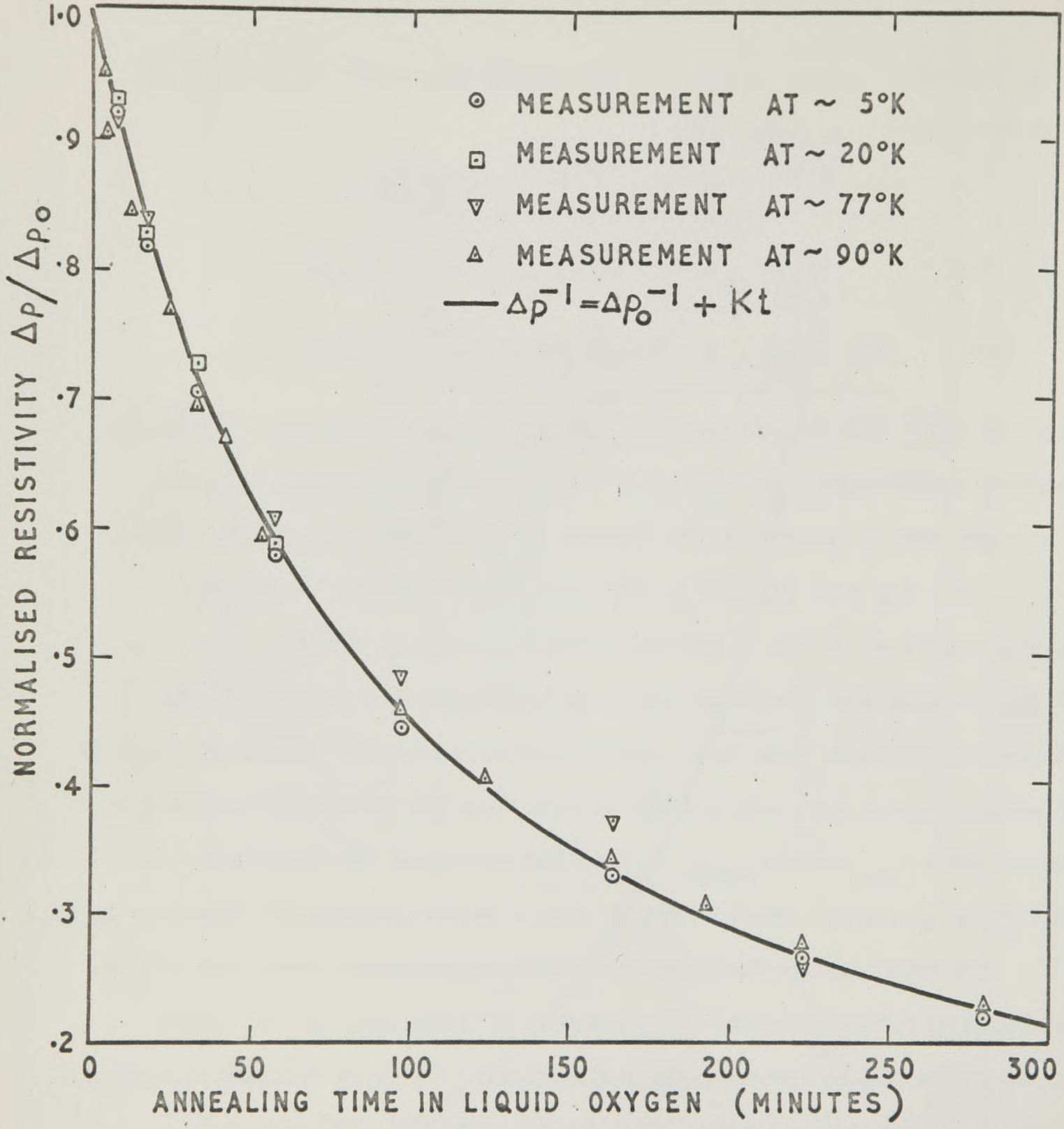


FIG.6.10 ANALYSIS OF RESULTS OF OXYGEN ANNEAL OF Pu 7.

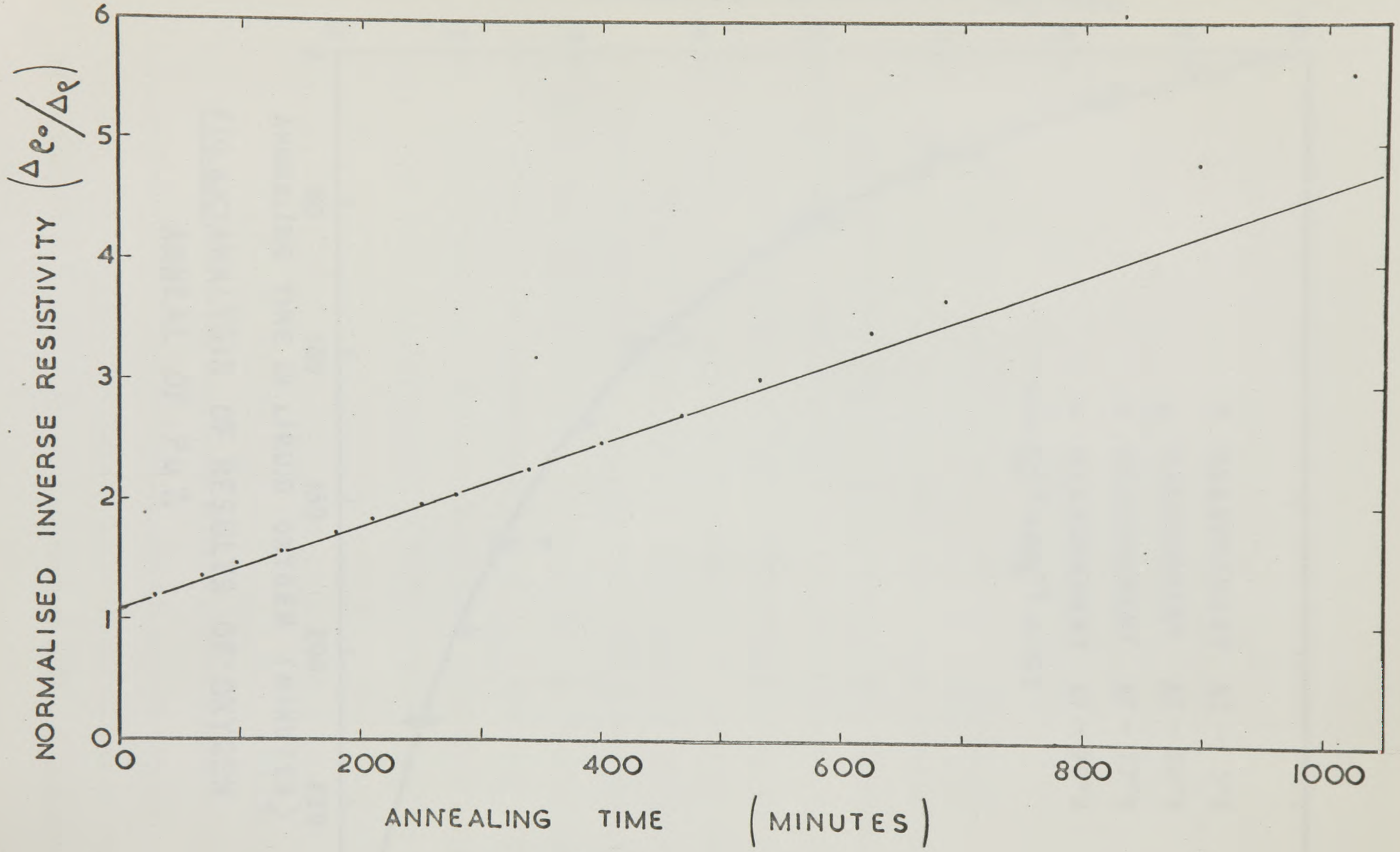


FIG. 6.11. ANALYSIS OF ~90°K ANNEAL OF $\alpha Pu2$ SHOWING THE LIMITED APPLICABILITY OF SECOND ORDER RATE KINETICS.

Having thus established that the resistivities measured during the $\sim 90^{\circ}K$ anneal of α Pu. 7 obeyed bimolecular rate Kinetics, the resistivities measured during the $\sim 90^{\circ}K$ anneal of α Pu. 2 were also analysed to see if they too obeyed second order Kinetics. From equation 6.x. for n = 2 we have

$$1/\Delta\rho = 1/\Delta\rho_0 + Kt \qquad \text{6.xiii.}$$

and hence a plot of $1/\Delta\rho$ against t will give a straight line if the anneal is of second order. Such a plot for the $\sim 5^{\circ}K$ resistivities measured during the $\sim 90^{\circ}K$ anneal of α Pu. 2 are shown in Fig.6.11. It can be seen that there is a linear relationship between $1/\Delta\rho$ and t for about 500 minutes but that at higher annealing times the value of $1/\Delta\rho$ exceeds that required for the linear relationship. As the annealing time increases the values of $\Delta\rho$ (= ρ measured - $\rho_{t\to\infty}$) become critically dependent on the value taken for ρ_∞. Unfortunately it is impossible to obtain accurate values of ρ_∞ by leaving the specimen at $\sim 90^{\circ}K$ for a long time as storage of α plutonium at $\sim 90^{\circ}K$ allows self-irradiation damage to build in at a slow rate with a consequent increase in $\rho_{5^{\circ}K}$ of about 1.5×10^{-2} $\mu\Omega$ cm/hr. It is therefore impossible to say whether the non linearity of the relationship between $1/\Delta\rho$ and t for large values of t is indicative of a change from second order rate Kinetics.

Finally we have also attempted to analyse the $\sim 77^{\circ}K$ anneal of α Pu. 7. However we have already shown that the $\sim 5^{\circ}K$ resistivity dropped 8.8 $\mu\Omega$ cm. in the first 6.5 minutes at $\sim 77^{\circ}K$ and then took a further 28 hours at $\sim 77^{\circ}K$ to drop another 9.4 $\mu\Omega$ cm. It is impossible

to reconcile these annealing rates with any normal rate Kinetics for a single annealing stage and it would seem that there should be a sub-stage present at a temperature lower than $\sim 77^{\circ}K$. As shown in Figs. 5.4. and 5.5. no such stage could be found by Isochronal annealing but there were not enough data points in the required temperature range definitely to rule out the possibility of a lower temperature annealing stage. In the absence of such data it was not considered worth carrying out a detailed analysis of the results of the $\sim 77^{\circ}K$ anneal of $\propto$ Fu. 7.

6.3. Determination of the Activation Energy Governing the $80^{\circ}K$ Annealing Stage

From equations 6.i. and 6.ii. we can obtain the expression

$$-dc/dt = f(c) K_0 e^{-E/kT} \qquad \text{6.xiv.}$$

and once more assuming that the resistivity change $\Delta\rho$ is proportional to c

$$-d\Delta\rho/dt = f(\Delta\rho) K_0 e^{-E/kT} \qquad \text{6.xv.}$$

The activation energy E can often be found without knowledge of the form of the function $f(\Delta\rho)$. Consider a specimen annealing isothermally at temperature T_1 and then suddenly raised to a higher temperature T_2 and annealed isothermally at this temperature. Then if the rate of change of $\Delta\rho$ just before the change of temperature is $(d\Delta\rho/dt)_1$ and just after it is $(d\Delta\rho/dt)_2$

we have

$$\frac{\left.\frac{d\Delta\rho}{dt}\right|_1}{\left.\frac{d\Delta\rho}{dt}\right|_2} = \frac{f(\Delta\rho) K_0 e^{-\frac{E}{kT_1}}}{f(\Delta\rho) K_0 e^{-\frac{E}{kT_2}}} \qquad \text{6.xvi.}$$

As the function $f(\Delta\rho)$ is the same for each temperature at the moment of change, it can now be cancelled leaving after simplification

$$\frac{\left.\frac{d\Delta\rho}{dt}\right|_1}{\left.\frac{d\Delta\rho}{dt}\right|_2} = e^{-\frac{E}{K}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} \qquad \text{6.xvii.}$$

Hence measuring $d\Delta\rho/dt$ just before and just after the temperature change allows E to be determined. One limitation of this method is, however, that E must be the same for both T_1 and T_2 and usually such temperature changes are small in order to meet this requirement.

Despite the doubt as to whether the same annealing stage, and activation energy, is operative for both the $\sim 77^{\circ}K$ and $\sim 90^{\circ}K$ anneals of α Pu. 7, we have calculated the activation energy by the above method as follows:

Rate of resistivity decrease at end of $\sim 77^{\circ}K$ anneal $= 1.2 \times 10^{-3}$ $\mu\Omega$ cm/min

" " " " " start of $\sim 90^{\circ}K$ " $= 1.37 \times 10^{-1}$ $\mu\Omega$ cm/min

Hence on sub.^{n} in eqn. 6.xvii.

$$\frac{1.2 \times 10^{-3}}{1.37 \times 10^{-1}} = 8.75 \times 10^{-3} = e^{\frac{-E}{8.616\times10^{-5}\left(\frac{1}{77}-\frac{1}{90}\right)}}$$

$$E = \frac{4.736 \times 8.616 \times 10^{-5}}{1.83 \times 10^{-3}} \text{ eV}$$

$$\underline{\underline{E = 0.22_3 \text{ eV}}}$$

A second method of calculating the activation energy of annealing processes has been given by Meechan and Brinkman (1956). A summary of their method is given in Appendix III. A strict application of their analysis would require two samples of similar chemical and physical

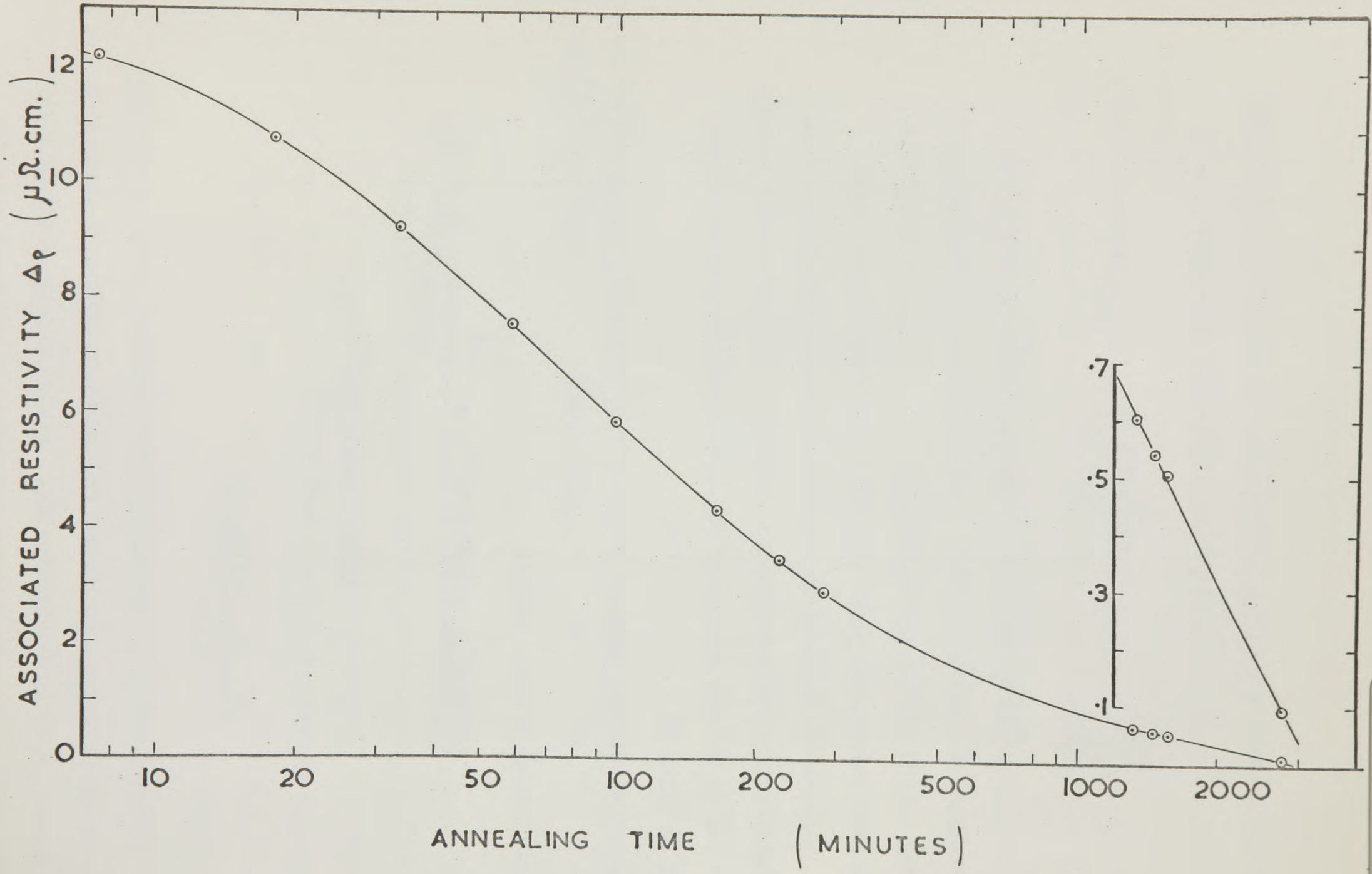


FIG. 6.12. ~5°K RESISTIVITY OF ∝ Pu.7 AS A FUNCTION OF ANNEALING TIME AT ~90°K

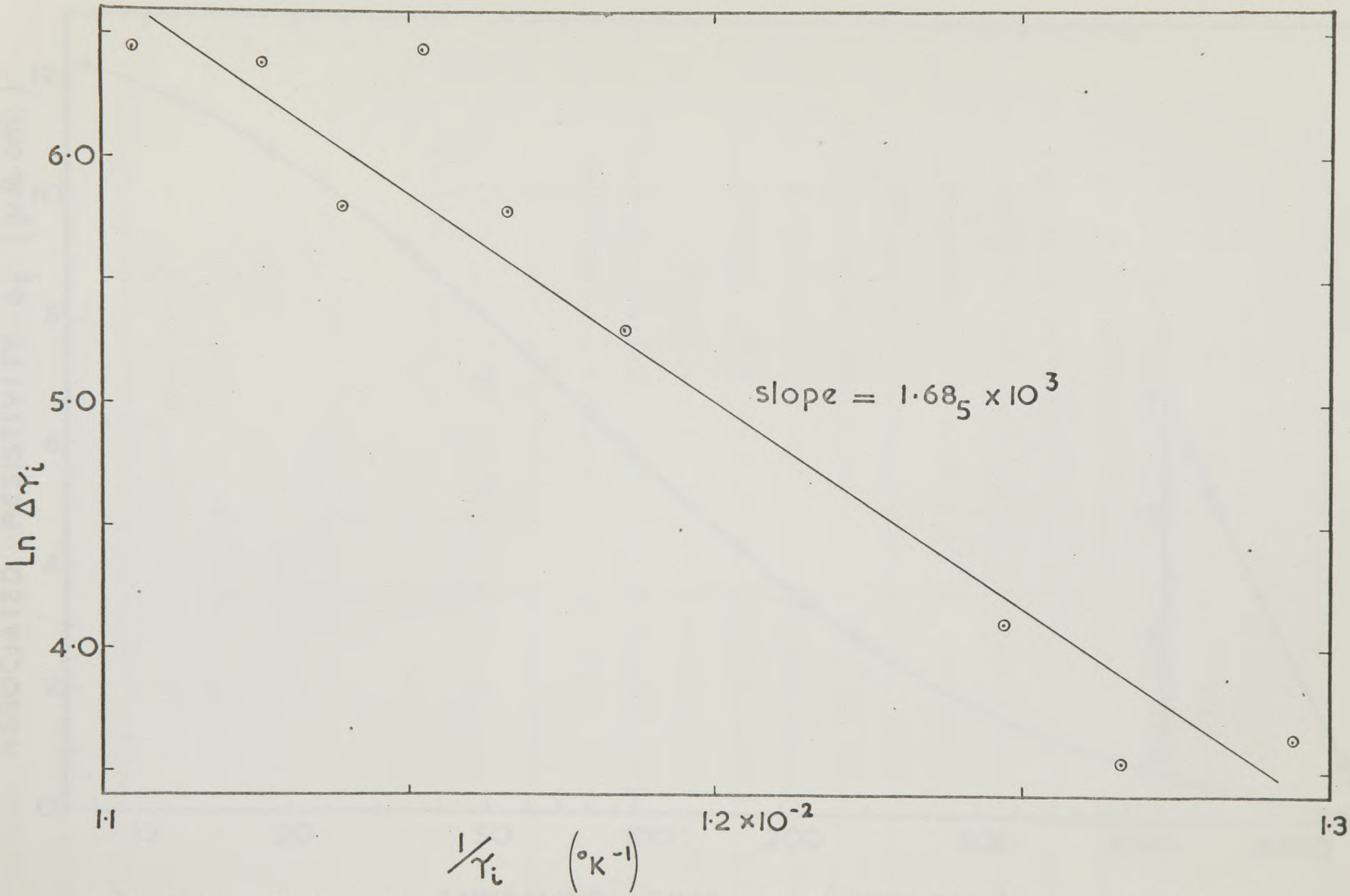


FIG. 6.13. DETERMINATION OF ACTIVATION ENERGY OF STAGE I RECOVERY OF α. PLUTONIUM BY THE METHOD OF MEECHAN AND BRINKMAN.

purity, although if the chemical rate equation,

$$-dc/dt = -K_0 c^n e^{-E/kT}$$

is valid for the annealing stage, the two samples need not have the same initial defect concentration. We have demonstrated that the $\sim 30^{\circ}K$ anneal of α Pu. 7 can be described fairly well by second order rate Kinetics, and we have used the above method to analyse the results of an isochronal anneal performed on α Pu. 6 and the $\sim 30^{\circ}K$ isothermal anneal of α Pu. 7, although α Pu. 7 was known to be considerably less pure than α Pu. 6. In Fig. 6.12. the resistivity associated with stage I annealing in α Pu. 7 is shown as a function of annealing time at $\sim 30^{\circ}K$ and has been corrected to allow for the effect of accumulation of self-damage due to storage at $\sim 30^{\circ}K$. In Table 6.B. the relevant isochronal annealing data of α Pu. 6 is shown together with the values of τ_i obtained from Fig. 6.11. Also shown in Table 6.B. are the values of $\ln \Delta\tau_i$ and $1/T_i$ which are used to plot Fig. 6.13.

The activation energy of the annealing process given by the slope of the line drawn through most of the points in Fig. 6.13 is then:

$$E = k. \frac{d(\ln \Delta\tau_i)}{d(1/T_i)} = 8.616 \times 10^{-5} \times 1.68_5 \times 10^3 = \underline{0.14_5}\ \underline{eV}$$

i.e. the activation energy E found by the method of Meechan and Brinkman is $\underline{E = 0.14_5\ eV}$. This compares with a value of $\underline{E = 0.22\ eV}$ found by the slope change method.

We consider that the agreement between these values is very good considering the crudeness of certain of the experimental arrangements, and the questionability of some of the assumptions made in deriving these values. Probably one of the most important assumptions made throughout

TABLE 6.B.

Relevant data from the isochronal anneal of α Pu. 6 and τ_i values taken from Fig.6.11

T anneal (°K)	$\Delta\rho$ ($\mu\Omega$ cm)	τ_i (min)	$\Delta\tau_i$	ln $\Delta\tau_i$	$1/T_i$
71.6	11.498	12.5			
			38	3.6376	.01294
77.3	8.024	50.5			
			34	3.5264	.01266
79.1	6.367	84.5			
			60.5	4.1027	.01247
81.2	4.697	145			
			200	5.2983	.01185
84.4	2.471	345			
			325	5.7839	.01166
85.75	1.363	670			
			630	6.4457	.01152
86.8	0.620	1300			
			330	5.7991	.01139
87.75	0.460	1630			
			590	6.3802	.01126
88.8	0.242	2220			
			630	6.4457	.01105
90.5	0.072	2850			

these analyses of annealing Kinetics has been the assumption that the resistivity change, $\Delta\rho$, used to follow the annealing process is proportional to c, the concentration of defects involved. Examination of any of the build in curves of α plutonium will show that $\Delta\rho$ is not a linear function of the holding time and hence of the number of defects produced. Whether in fact $\Delta\rho$ is proportional to the concentration of defects stored, c, and the curvature of the $\Delta\rho$ vs. t curves shows that not all of the defects produced are stored, depends fundamentally on the model used to interpret the whole phenomenon of self-irradiation damage in plutonium. This subject will be discussed in the final chapter.

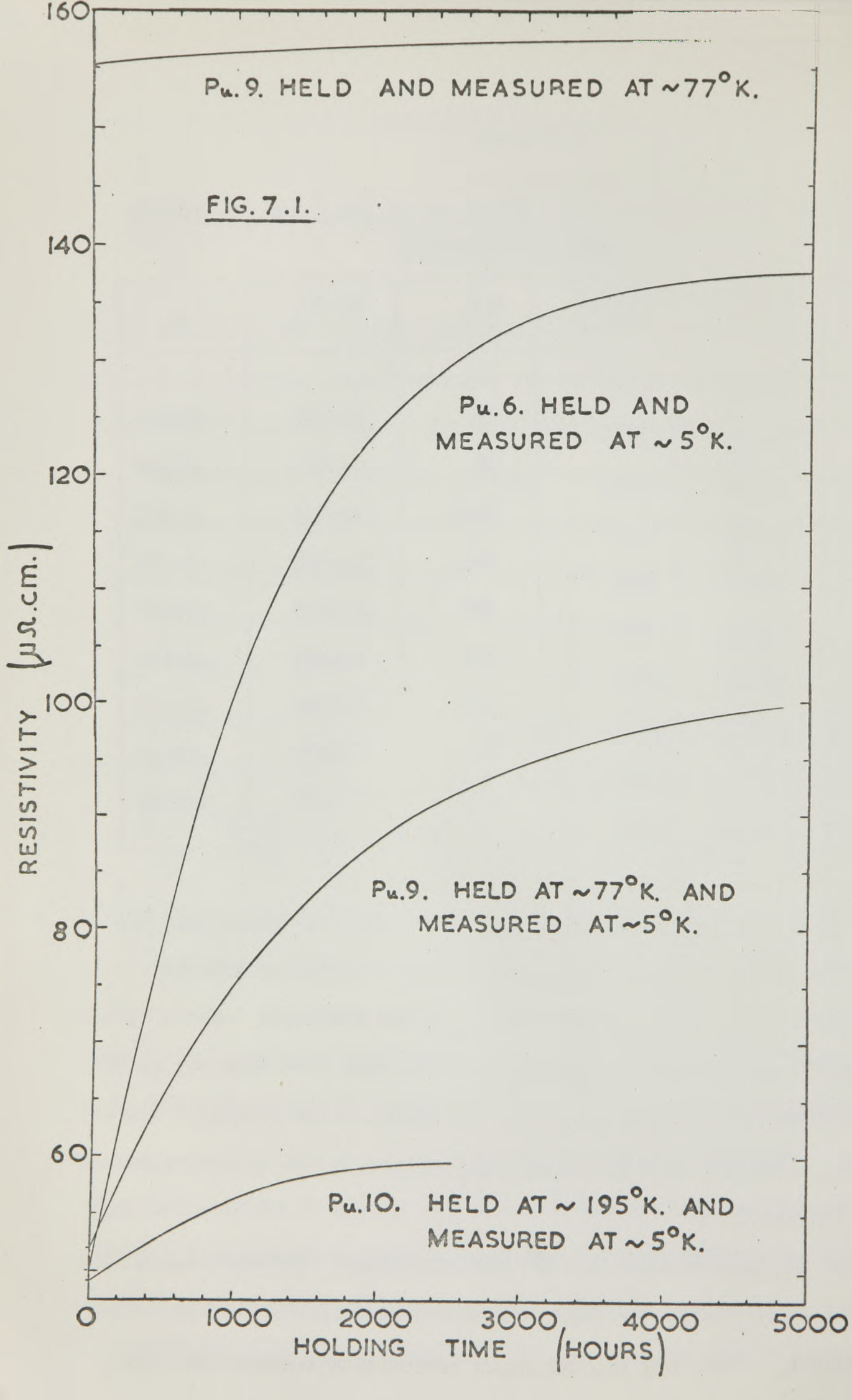

Pu. 9. HELD AND MEASURED AT ~77°K.
Pu.6. HELD AND MEASURED AT ~5°K.
Pu.9. HELD AT ~77°K. AND MEASURED AT ~5°K.
Pu.10. HELD AT ~195°K. AND MEASURED AT ~5°K.
RESISTIVITY (μΩ.cm.)
160
140
120
100
80
60
0
1000
2000
3000
4000
5000
HOLDING TIME (HOURS)

FIG. 7.1.

CHAPTER 7

Other Experimental Results

So far we have described the way in which the resistivities of alpha and delta stabilised plutonium increase when held at or below $\sim 20^{\circ}K$ and the ways in which this additional resistivity is recovered by Isochronal and Isothermal annealing. In this chapter we shall describe other experiments performed by us relating to these subjects, but which do not fit neatly into any of the earlier chapters.

7.1. Further Self-Irradiation Experiments on Alpha Plutonium

The most important of these results are those in which samples of alpha plutonium were held at fixed temperatures higher than those used in the earlier chapters but still below room temperature. In Fig. 7.1 we show how the measured resistivities of samples held in liquid nitrogen and solid carbon dioxide change with time; the behaviour during liquid helium holding is also shown for comparison. All three specimens were made from the same length of extruded wire and hence are, for practical purposes, identical as far as chemical and isotopic composition are concerned. The slight variation of initial resistivity measured at $\sim 5^{\circ}K$ indicates either a change in physical purity of the specimens or represents the error in form factor used in calculating the resistivities from the measured resistances.

The experiments were carried out as follows: for the liquid nitrogen irradiation the specimen was cooled in stages from room temperature to $\sim 5^{\circ}K$ and its undamaged resistivity measured at ~ 290,

~273, ~195, ~90, ~77, ~20 and ~5°K. It was then transferred to a dewar of liquid nitrogen and held at this temperature. Periodically the resistivity at 77°K was measured, after which the specimen was quickly transferred to a dewar of liquid helium. After allowing time for temperature equilibrium to be established, the resistivity was measured at ~5°K and the specimen then returned to liquid nitrogen. In this way the effect of storage at ~77°K was followed by measuring the resistivities both at ~77°K and ~5°K.

The ~195°K irradiation was carried out in a similar manner, with storage in solid carbon dioxide and periodic measurements at ~195, ~77, and ~5°K. Owing to rather poor experimental conditions no consistant pattern emerged from the readings taken at ~195°K and ~77°K, however a steady increase in the ~5°K resistivity was found as shown in Fig. 7.1. From the liquid nitrogen irradiation it was found that there was a steady increase in both the resistivity measured at ~77°K and at ~5°K, the initial rate of resistivity increase at ~77°K being about 1/20th of the rate measured at ~5°K.

In Table 2.A. the average rates of resistivity increase measured at ~5°K during the first 1,000 hours irradiation at ~5°K, ~77°K and ~195°K are given, and are also shown as a percentage of the rate of 5°K resistivity increase during ~5°K irradiation.

From Fig. 5.2., Chapter 5, it can be seen that after irradiation at ~5°K and then annealing isochronally, about 47% of the initial resistivity increase remains after completely annealing the first stage to ~90°K, and about 20% of the initial increase remains after completely annealing the second stage to ~200°K. It would thus appear

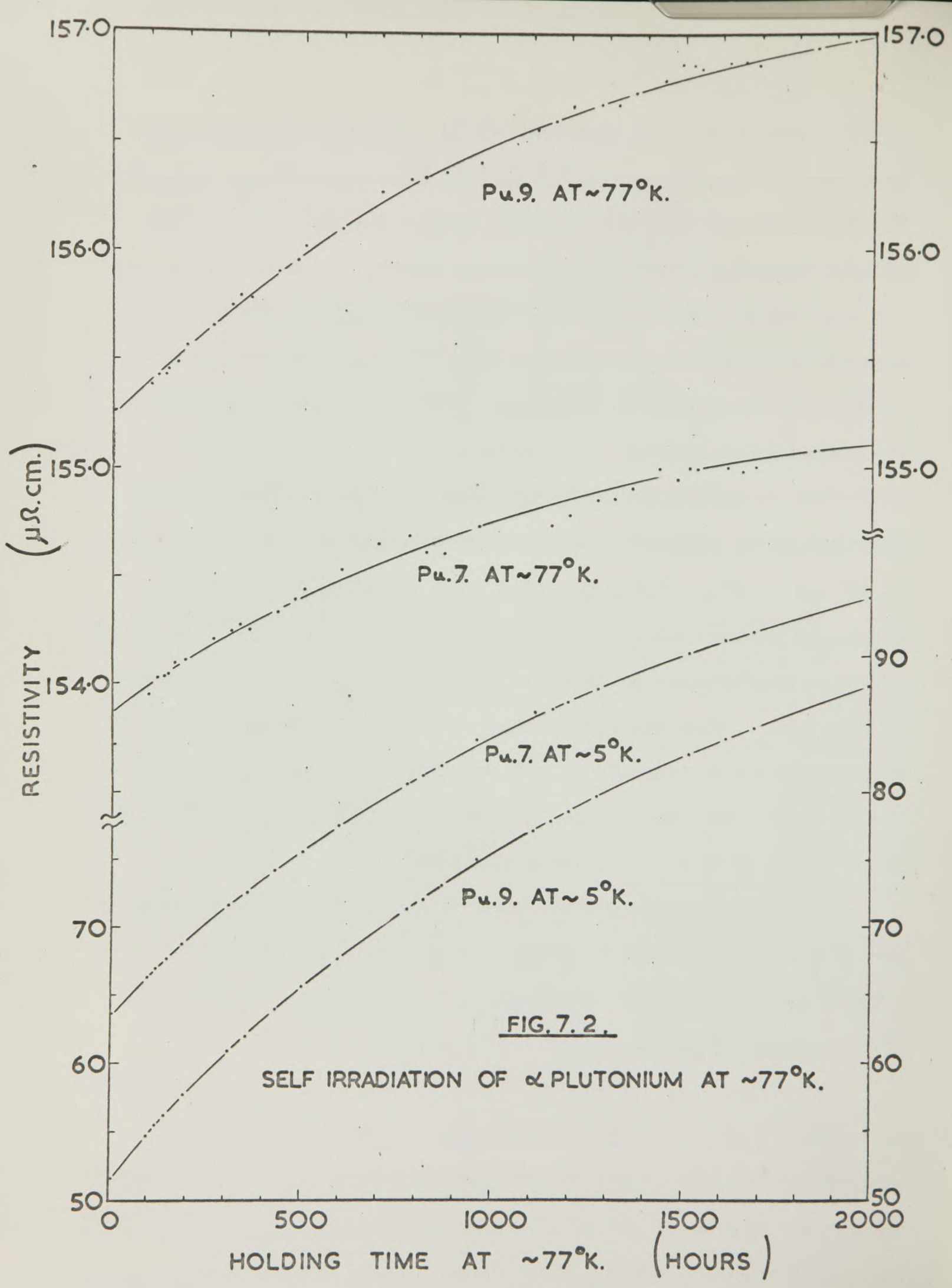


FIG. 7.2.

SELF IRRADIATION OF α PLUTONIUM AT ~77°K.

TABLE 7.A.

Irradiation Temperature (T°K)	Average rate of increase of ~5°K resistivity during first 1,000 hours irradiation at T ($\mu\Omega$ cm/hr)	Ratio of rates of resistivity increase during irradiation at T°K and 5°K.
5	5.17×10^{-2}	100%
77	2.36×10^{-2}	45.5%
195	7.2×10^{-3}	14%

that, as expected, irradiation at the higher temperatures produces a similar effect to irradiation at low temperatures and annealing those defects not stable at the higher temperatures.

In chapter 6, we showed that after long periods of self-irradiation at ~5°K the resistivity measured at ~5°K had risen while the resistivities measured at ~77°K and ~90°K had fallen towards the same value. However, as we have just shown, self-irradiation at ~77°K causes both the resistivity measured at 5°K and at ~77°K to rise. These results are shown in more detail in Fig. 7.2. Pu. 7 and Pu. 9 both have similar self heats, but Pu. 7 is considerably less pure than Pu. 9. The less pure Pu. 7 has a higher initial ~5°K resistivity and a lower ~77°K resistivity than the purer Pu. 9, a feature upon which we shall comment later. This difference in purity also affects the self-irradiation induced resistivity changes, especially those measured at ~77°K. The ~77°K resistivity of Pu. 7 increased from 153.88 $\mu\Omega$cm. to 155.11 $\mu\Omega$cm., a difference of 1.23 $\mu\Omega$cm. in 2,000 hours, compared with an increase of 1.80 $\mu\Omega$cm. from 155.20 to 157.00 $\mu\Omega$cm. for Pu. 9. After almost 5,000 hours in liquid nitrogen the resistivity of Pu. 9 had risen to ~ 157.6 $\mu\Omega$cm. and appeared to be approaching a saturation value of about 157.8

$\mu\Omega$cm. This is very similar to the resistivity of the 105°K maximum in the undamaged specimen and it would appear that the effect of self-irradiation in liquid nitrogen is to increase the 77°K resistivity to the value of the undamaged resistivity maximum. The data from Fig. 7.2. is summarised in Table 7.B.

TABLE 7.B.

Sample	Initial resistivity ($\mu\Omega$cm.)	Probable asymptote ($\mu\Omega$cm.)	Initial rate of resistivity increase ($\mu\Omega$cm/hr.)
Pu.9 at 5°K	51.65	101	3.3×10^{-2}
Pu.9 at 77°K	155.35	157.8	1.65×10^{-3}
Pu.7 at 5°K	63.55	(105)	3.0×10^{-2}
Pu.7 at 77°K	153.85	(155.3)	1.31×10^{-3}

We are thus confronted with two apparently contradictory results; that self-irradiation at very low temperatures produces a large decrease in the measured resistivity at ~77°K, whereas self-irradiation at ~77°K produces a slight increase in the resistivity measured at ~77°K. We can offer no firm explanation for these results but they will be discussed further in the concluding chapter.

7.2. Quenching Experiments on Alpha Plutonium

At an early stage in our investigation of the self-irradiation properties of alpha plutonium it was considered possible that the negative temperature coefficient of resistivity above ~100°K might be explained as due to a dynamic balance between the rate of production and the rate of annealing of defects. The self heat, and hence rate of

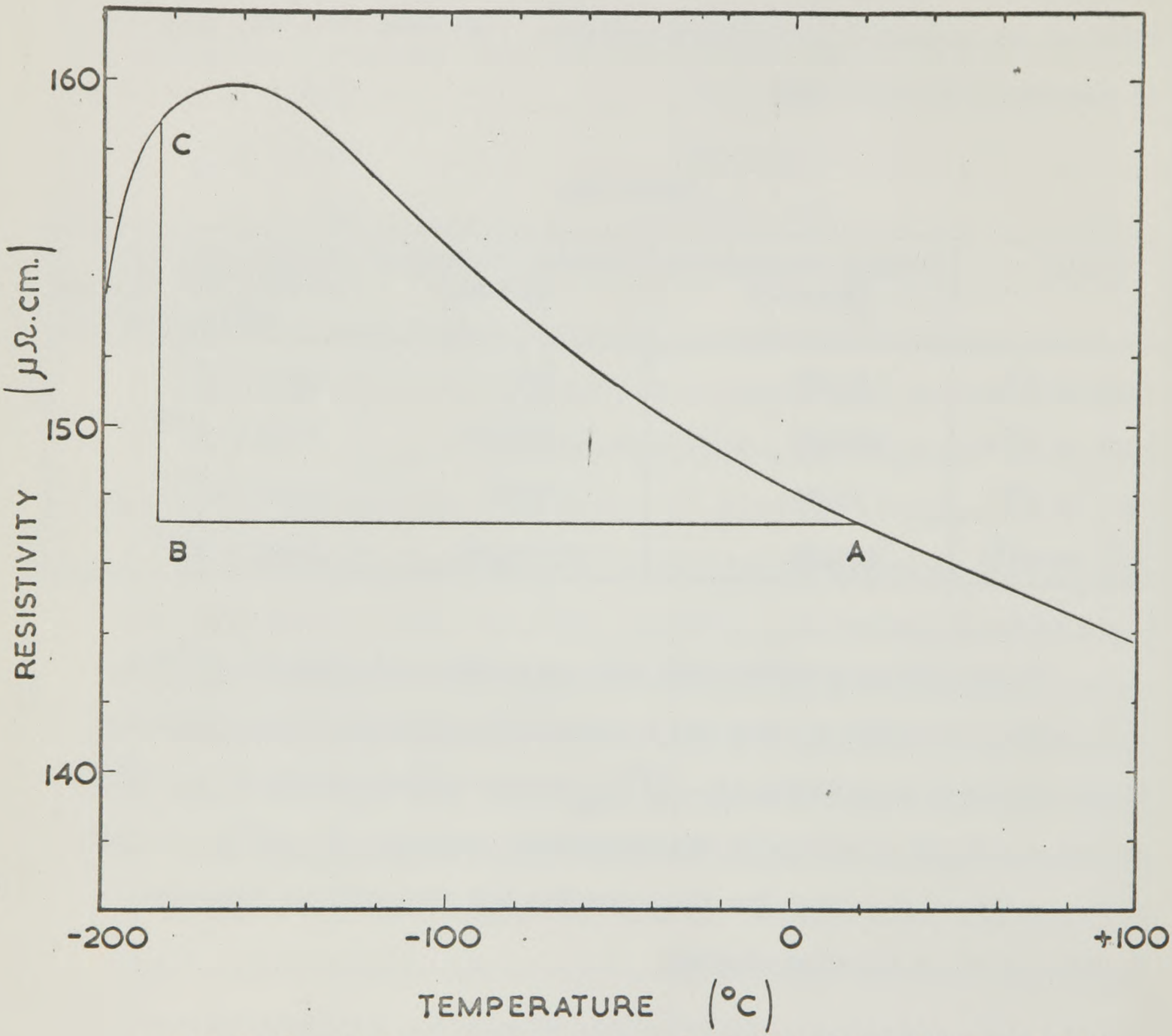


FIG. 7.3. ALPHA PLUTONIUM : QUENCH TO LIQUID ARGON.

production of defects, is temperature independent but it was known that more defects were stored at low temperatures than at room temperature. If the negative temperature coefficient were caused by this process, quenching from room temperature, the point A in Fig. 7.3., to liquid argon, the point B, would leave the specimen with a deficiency of stored defects compared with its equilibrium concentration. A rise in resistivity from B to C would then be expected as more defects accumulated. When a specimen was quenched from room temperature to a liquid argon bath the resistivity rose to within 1 part in 10^3 of its equilibrium value C within one minute, while simultaneous measurements from a thermocouple attached to the specimen showed that it required the same time interval to reach its equilibrium temperature. From this result we conclude that the cause of the negative temperature coefficient of resistivity is not due to an equilibrium between the creation and annealing of defects. Furthermore from the isochronal annealing results of chapter 5 one would expect to see some indication of the $\sim 200^{\circ}K$ annealing stage in the resistance-temperature curve if the negative temperature coefficient were due to that cause. Quenching experiments from room temperature to $\sim 5^{\circ}K$ have also shown that there is no time lag greater than that required for the establishment of temperature equilibrium before the resistivity reaches its equilibrium value. Similarly there is no difference between the $\sim 5^{\circ}K$ resistivity of specimens thus quenched and specimens cooled over a period of about an hour. We are satisfied that such results do not support the theory put forward by Sandenaw and Olsen (1960) of an atomic order-disorder transformation at $\sim 50^{\circ}K$.

7.3. Magnetoresistance in Plutonium

In view of the antiferromagnetic theories put forward to explain the low temperature behaviour of plutonium, we decided to measure the magneto-resistivity of α Pu. 8, one of our high purity samples, at low temperatures. This was done with a canned sample using the narrow tailed metal dewar and magnet shown in Fig. 2.1. With this apparatus it was possible to obtain a 10 Kilogauss field with a pole piece separation of 3 cm. No magneto-resistance was reliably detected to within the limits shown in Table 7.C.

TABLE 7.C.

Temperature °K	Limit of Reliable Detection
~ 77	1 part in 2.5×10^4
~ 20	1 part in 8.0×10^3
~ 5	1 part in 4.5×10^3

The limit decreased at low temperatures because in all cases the potentials recorded were only accurate to the nearest 0.1 μV. Such changes as were detected at ~ 5°K and ~ 20°K were positive, i.e. there was a very slightly higher resistance in the presence of the magnetic field. We do not, however, consider that these indications were reliable. There was definitely no negative magneto-resistance as might have been expected for an antiferromagnetic.

7.4. The Effect of Purity on the Low Temperature Resistivity of Alpha Plutonium

Olsen and Elliott (1962) have reported that at very low temperatures

the resistivities of impure specimens are in general higher than those of purer specimens, but at higher temperatures this tendency is reversed and the purer specimens have the higher resistivities. A similar effect had been noticed with our specimens and in Table 7.D. we give the measured values of some of our specimens at temperatures ranging from ~5°K to room temperature.

TABLE 7.D.

Specimen	Resistivity in $\mu\Omega$ cm. at: 273°K	195°K	90°K	77°K	20°K	5°K
Pu. 11	152.01	-	161.97	159.07	39.17	18.24
Pu. 8	151.34	155.78	162.47	159.87	49.27	29.21
Pu. 2	149.68	154.12	160.08	158.94	67.02	47.23
Pu. 9	148.38	152.73	157.05	154.52	68.91	50.66
Pu. 7	146.04	150.27	153.59	151.05	74.69	56.56

The absolute values quoted in Table 7.D. are uncertain to the extent of the error in the form factor which is of the order of 1%. It can however be seen that in general the less pure specimens have higher resistivities at temperatures below ~ 50-60°K, and lower resistivities above this temperature. This shows a similar pattern to that found after self-irradiation at ~5°K, i.e. that the resistivity below ~ 50°K had increased while that above ~50°K had decreased. In their paper Olsen and Elliott, (1962) quote a temperature of~ 100°K for this inversion of resistivity changes. Closer examination of their results, however, shows that inversion actually took place at ~ 50-60°K in agreement with our findings.

7.5. Self-Irradiation in other Alpha Active Metals

We have carried out preliminary experiments on the self-irradiation damage behaviour of two other alpha active materials, Uranium 233 and Neptunium 237. Protoactinium 231 would also prove suitable for this type of work when available in the metallic form, as would Americium 241 if the problems associated with its extremely high gamma activity could be solved. In Table 7.5. we give the calculated self heats of these isotopes together with that of the common isotopes of plutonium. The self heats have been calculated from the half-lives and alpha particle energies given in a review by Stroninger, Hollander and Seaborg (1958). The mean alpha particle energies and the energy of the recoil nucleus have been used in the calculations but the beta and gamma energies have been neglected.

TABLE 7.5.

Isotope	Disintegration Energy (neglecting β's and γ's) (MeV)	Half Life (years)	Self Heat (mW/gm)
Pa. 231	4.522	3.43×10^4	1.209
U. 233	4.892	1.62×10^5	0.275
Np. 237	4.857	2.20×10^6	0.0197
Pu. 238	5.577	8.7	570
Pu. 239	5.227	2.436×10^4	1.901
Pu. 240	5.239	6.58×10^3	7.025
Pu. 241	4.976	(13)	(13.45)
Am. 241	5.556	458	106.6

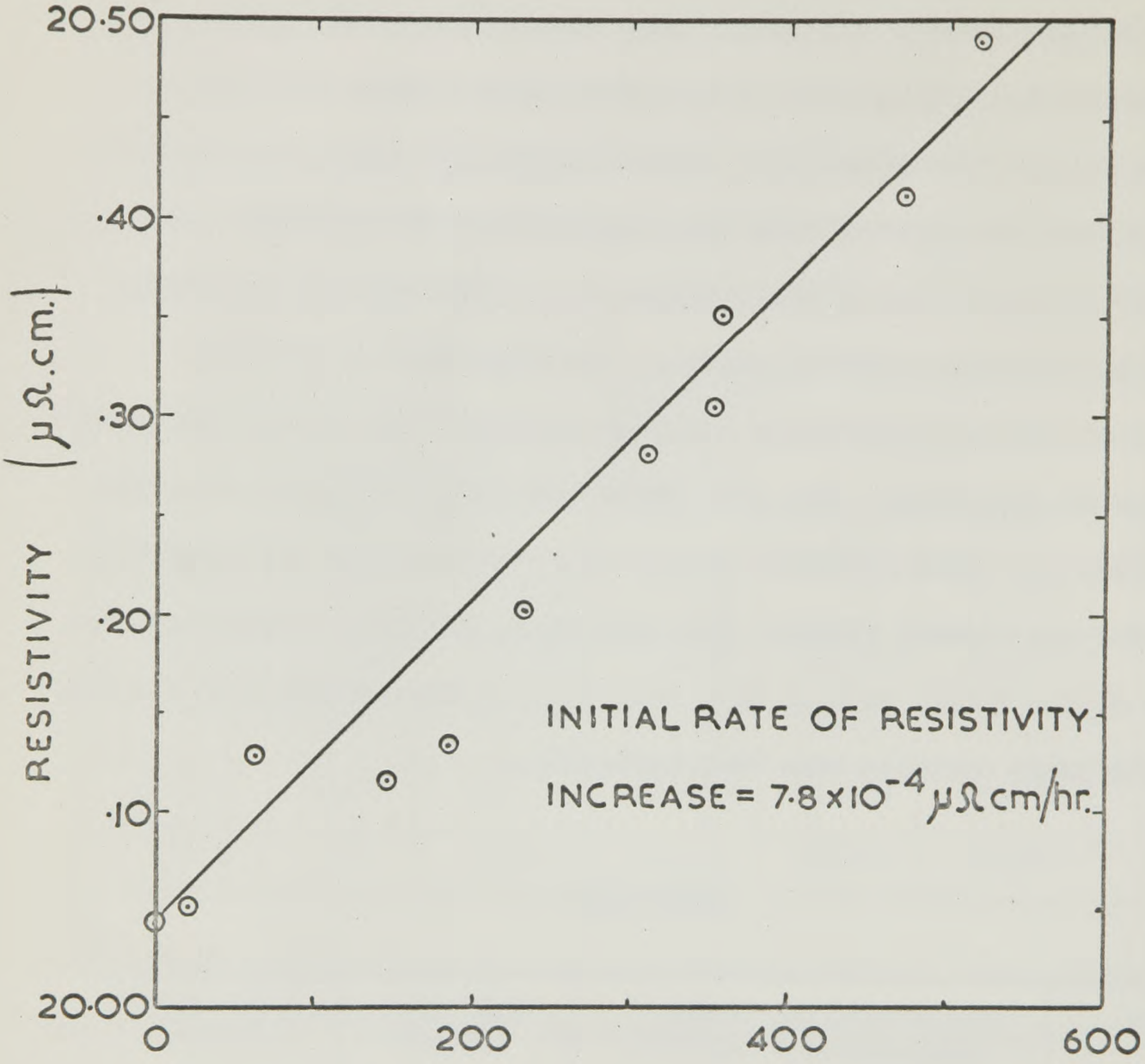


FIG. 7.4. SELF-IRRADIATION DAMAGE INDUCED CHANGES IN THE RESISTIVITY OF URANIUM 233 HELD AT ~5°K.

We have doubts about the accuracy of the calculated value for Pu. 241 because it is highly β active and only 4×10^{-3}% of its decays result in α emission. We have therefore multiplied the half life of 13 years by 4×10^{-3} to give an effective half life. This may be in error.

It can thus be seen that the self heats of U. 233 and Np. 237 are respectively about 1/10th and 1/100th of that of a typical plutonium specimen. In consequence proportionately lower rates of resistivity increase might be expected when these isotopes are held at low temperatures. In Fig. 7.4. the resistivity of a sample of U. 233 is shown as a function of time held in liquid helium. The initial rate of resistivity increase of 7.8×10^{-4} $\mu\Omega$ cm/hr. is as expected considerably lower than that of typical plutonium specimens. The run was abandoned after about 600 hours in liquid helium because of a failure of the lead insulation. It will be noticed from Fig. 7.4. that there is considerable scatter of the results about the line shown. This occurred because the measured potential of ~ 420 μV was increasing at a rate of only ~ 1.5 μV/100 hours, which was little more than the random error associated with the measuring system. The specimen used was unfortunately very small because there was very little U. 233 available for experimental purposes. In order to obtain as advantageous a form factor as possible the specimen was made as thin and long as practicable, it was still, however, only 5.5 mm. long. Its cross sectional area was found by measuring its volume and density by weighing and then dividing the volume by the length. The form factor thus calculated was probably only accurate to about ± 25% and hence the resistivities quoted are subject to the same error.

Although the neptunium specimen used for self-irradiation

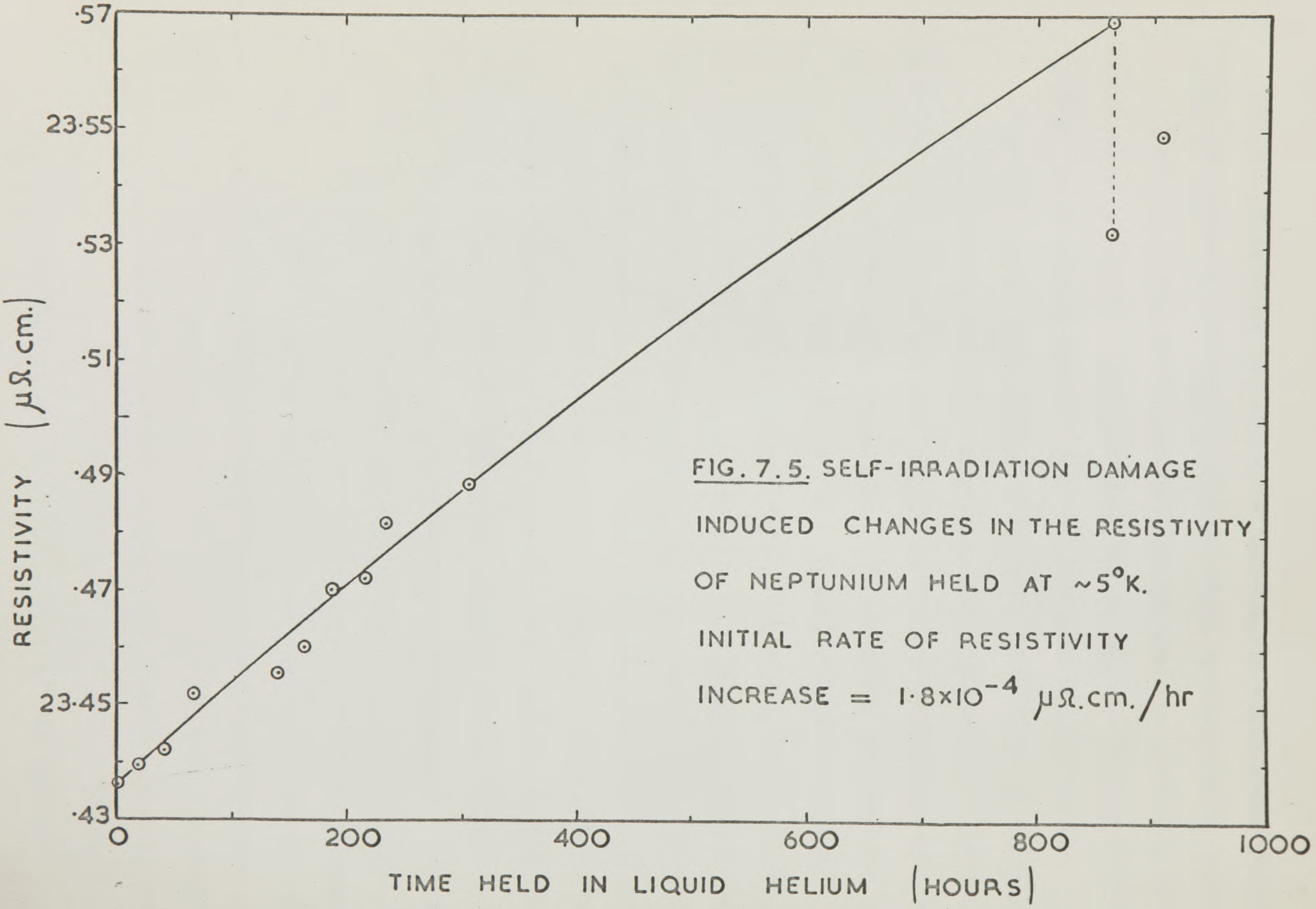


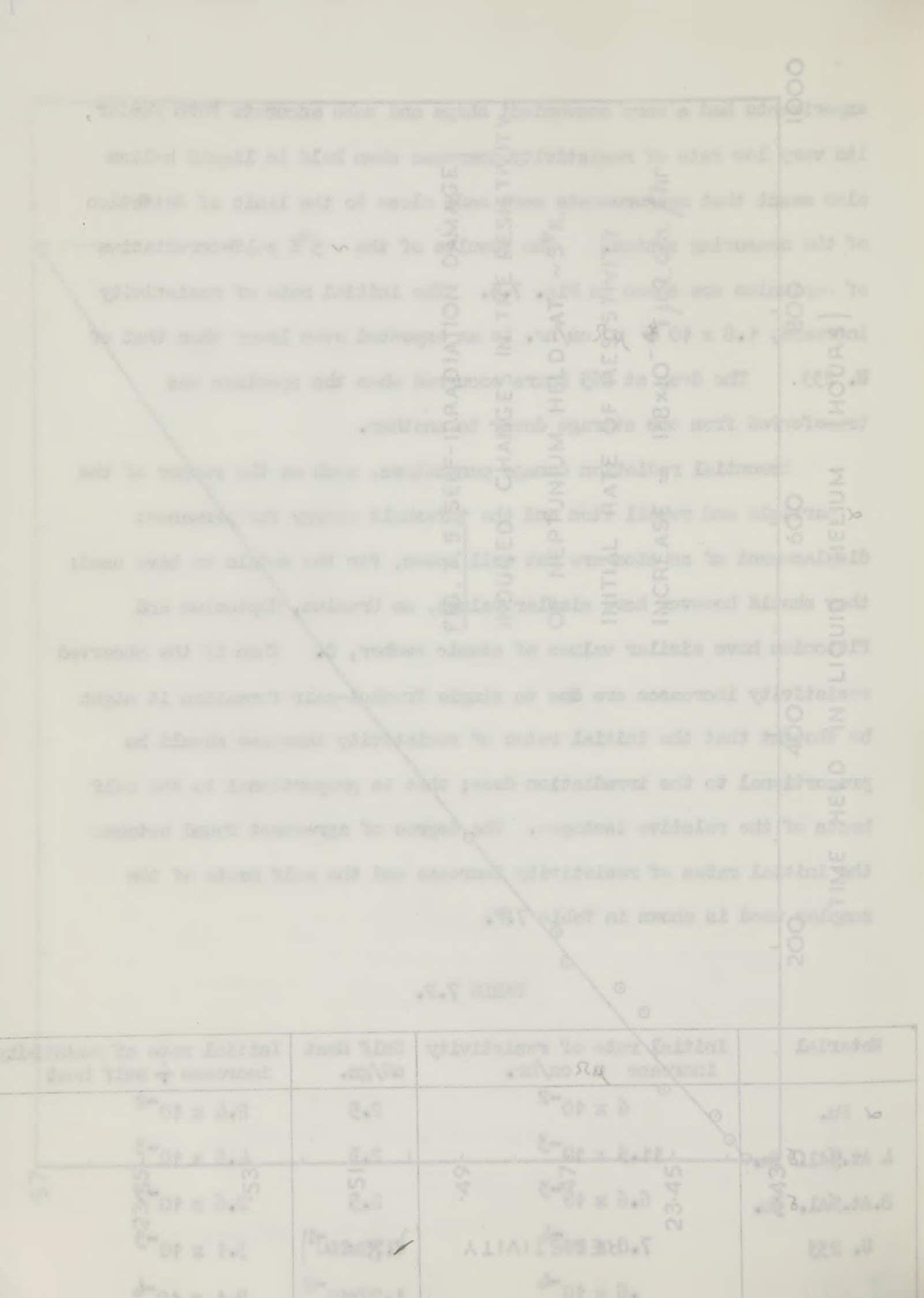
FIG. 7.5. SELF-IRRADIATION DAMAGE INDUCED CHANGES IN THE RESISTIVITY OF NEPTUNIUM HELD AT ~5°K. INITIAL RATE OF RESISTIVITY INCREASE = $1 \cdot 8 \times 10^{-4}$ μΩ.cm./hr

experiments had a more convenient shape and more accurate form factor, its very low rate of resistivity increase when held in liquid helium also meant that measurements were made close to the limit of detection of the measuring system. The results of the ~ 5°K self-irradiation of neptunium are shown in Fig. 7.5. The initial rate of resistivity increase, 1.6×10^{-4} $\mu\Omega$cm/hr. is as expected even lower than that of U. 233. The drop at 865 hours occurred when the specimen was transferred from one storage dewar to another.

Essential radiation damage parameters, such as the ranges of the α particle and recoil atom and the threshold energy for permanent displacement of an atom are not well known, for the metals we have used; they should however have similar values, as Uranium, Neptunium and Plutonium have similar values of atomic number, Z. Then if the observed resistivity increases are due to simple Frenkel-pair formation it might be thought that the initial rates of resistivity increase should be proportional to the irradiation dose; that is proportional to the self heats of the relative isotopes. The degree of agreement found between the initial rates of resistivity increase and the self heats of the samples used is shown in Table 7.F.

TABLE 7.F.

Material	Initial rate of resistivity increase $\mu\Omega$cm/hr.	Self Heat mW/gm.	Initial rate of resistivity increase $\div$ self heat
α Pu.	6×10^{-2}	2.5	2.4×10^{-2}
4 At.%Al.δ Pu.	11.5×10^{-3}	2.5	4.6×10^{-3}
8.At.%Al.δ Pu.	6.6×10^{-3}	2.5	2.6×10^{-3}
U. 233	7.8×10^{-4}	2.75×10^{-1}	3.1×10^{-3}
Np. 237	1.8×10^{-4}	1.97×10^{-2}	9.1×10^{-4}


INCREASE OF INITIAL RADIATION CHARGE
INCREASE OF INITIAL RADIATION CHARGE
INCREASE OF INITIAL RADIATION CHARGE

It can be seen that agreement is not very good, especially between alpha and delta stabilised plutonium.

A rule of thumb proposed by Walker (Lucasson and Walker (1962)) states that a 1% concentration of Frenkel pairs produces a resistivity change in a metal equal to the difference between its resistivity at 273°K and its residual resistivity. Once again without prior knowledge of the number of Frenkel pairs produced per α disintegration in the isotopes used, and without an independent assessment of what constitutes a 1% concentration of Frenkel pairs, accurate comparisons are not possible. However, if we assume that the rate of production of Frenkel pairs is proportional to the self heat, which in view of the similarity of Z for uranium, neptunium and plutonium is not unreasonable, then Walker's rule leads to the relation:

$$\frac{\text{Initial rate of resistivity increase}}{\text{Self Heat} \times (\text{Resistivity at } 273^{\circ}\text{K} - \text{Residual resistivity})} = \text{constant.K}.$$

In Table 7.6. we show the values obtained for this constant from a number of our specimens. It can be seen that there is reasonable agreement between the values of the constant K calculated for the different specimens, although once again there is not very good agreement between the values for the two δ plutonium specimens. We shall comment further upon Walker's rule in the final chapter.

For Table 7.6 see over.....

TABLE 7.6.

Sample	Initial rate of resistivity increase $\frac{d\rho}{dt}\Big\|_0$ ($\mu\Omega$ cm/hr.)	$\rho_{273}-\rho_0$ ($\mu\Omega$ cm.)	Self Heat (mW/gm.)	$K = \frac{d\rho}{dt}\Big\|_0 \Big/ \text{self heat} \times (\rho_{273}-\rho_0)$
α Pu. 5	5.25×10^{-2}	104.32	2.124	2.37×10^{-4}
α Pu. 6	$7.07_5 \times 10^{-2}$	100.23	2.894	2.48×10^{-4}
α Pu. 7	6.18×10^{-2}	89.48	2.810	2.46×10^{-4}
α Pu. 8	6.06×10^{-2}	122.126	2.458	2.02×10^{-4}
δ Pu. 4	11.5×10^{-3}	27.84	2.02_5	2.04×10^{-4}
δ Pu. 12	6.6×10^{-3}	5.15_5	1.940	6.60×10^{-4}
U. 233	7.8×10^{-4}	29.23	2.75×10^{-1}	$9.7_0 \times 10^{-5}$
Np. 237	1.8×10^{-4}	81.52	1.97×10^{-2}	1.12×10^{-4}

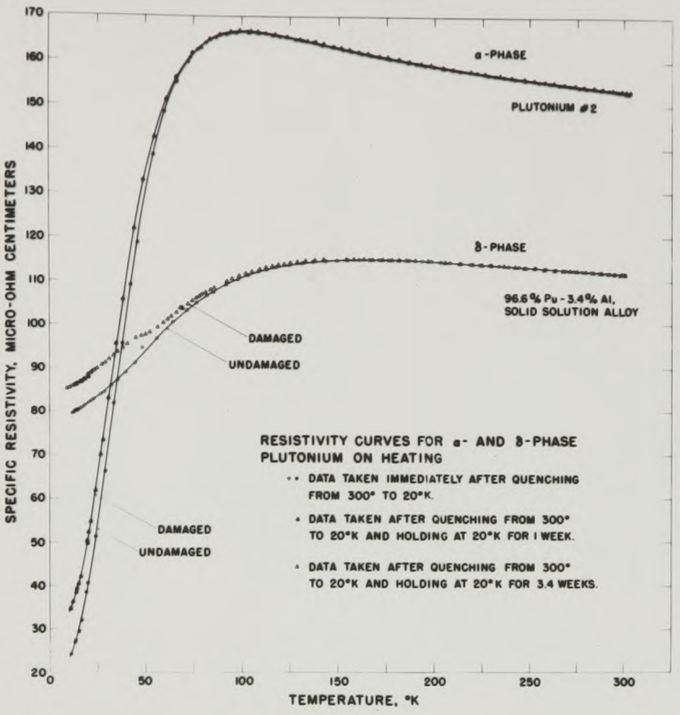
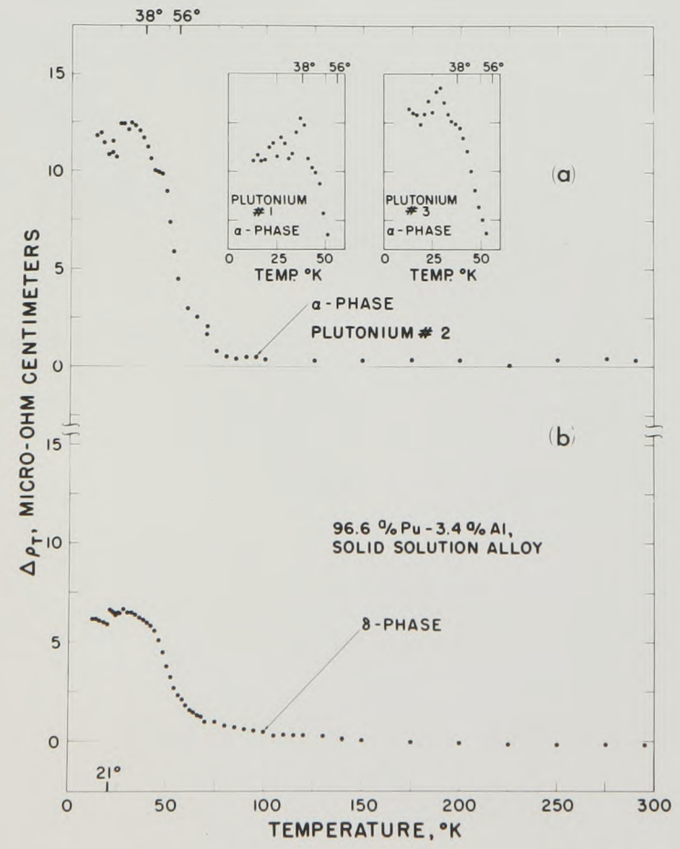


FIG. 8.1



ANNEALING OF SELF-IRRADIATION DAMAGE IN PLUTONIUM

FIG. 8.2

CHAPTER 8

Further results on the self-irradiation of plutonium and its delta alloys

In this chapter we shall present the results obtained by other workers on the effects of low temperature self-irradiation damage on the physical properties of plutonium. Immediately relevant comparisons with our own work will be made but further discussion will be left until the final chapter.

8.1. Electrical Resistivity measurements

We have already dealt in Chapter 3 with the discrepancy between our initial rates of resistivity increase at 5°K and 20°K and those of Olsen and Elliott (1962), and have shown that it arose because of the difference in purity of the plutonium used by the two laboratories. In a later paper, Olsen, Elliott and Sandenaw (1962) presented information on the annealing behaviour of α and δ stabilised plutonium which is shown in Figs. 8.1 and 8.2 a & b. In Fig. 8.1 the resistivities of a specimen of α plutonium and a 3.4 At.% Al. δ stabilised alloy are shown during slow warming both in the undamaged state and after holding for some time at ~ 20°K. In Figs. 8.2 a & b the difference between the undamaged and damaged curves, $\Delta\rho_T$, at any temperature T, is shown as a function of T. This analysis corresponds quite closely to that given by us in Figs. 3.5 and 3.6 for α plutonium and in Fig. 4.5. for δ stabilised plutonium. Only below ~ 40°K for α plutonium and ~ 35°K for 3.4 At.% Al. δ stabilised plutonium can comparisons be made between

our data and that of Olsen and Elliott as we have shown that pronounced annealing sets in above these temperatures. Below these temperatures Figs. 8.2 a & b show the temperature dependence of the additional resistivity produced by self-irradiation damage, and are in broad agreement with our results. We did not, however, find any sign of the dip in the $\Delta\rho_T$ vs. T curve at ~ 20°K found by Olsen and Elliott and which they attribute to the same cause as as the dips observed in the thermal recovery of deuteron bombarded gold (Cooper, Koehler & Marx (1955)). Above ~40°K for α and ~35°K for δ plutonium the $\Delta\rho_T$ vs. T curves show the combined effects of the temperature dependence of the additional resistivity and of the change in additional resistivity due to annealing. In the same paper annealing data is presented which was obtained by measurement at ~ 20°K, slowly warming (0.1 to 0.2°K/minute) to a range of annealing temperatures, holding for up to 30 minutes at the annealing temperature, quenching back to 20°K and then remeasuring the resistivity at~20°K.

This data is given in Table 8.A.

Comparisons with our isochronal annealing data presented in Chapter 5 are made difficult for two reasons: firstly their data was taken after extremely slow warming to the annealing temperature, whereas our specimens were warmed as quickly as possible, secondly it can be seen from Table 8.A. that quite large amounts of damage built in between successive annealing runs thus confusing the annealing spectrum. Their results do show however that strong annealing occurs at ~ 30°K and above.

In comparing their two sets of annealing data, that of Figs. 8.2 a and b and Table 8.A, Olsen and Elliott note that from Fig. 8.2a, ~ 80% of

TABLE 8.A.

T anneal (°K)	$\Delta\rho$ before anneal ($\Delta\rho_o$) ($\mu\Omega$ cm.)	$\Delta\rho$ after anneal ($\Delta\rho'$) ($\mu\Omega$ cm.)	Difference $\Delta\rho_o - \Delta\rho'$ ($\mu\Omega$ cm.)	Percentage Decrease $\frac{\Delta\rho_o - \Delta\rho'}{\Delta\rho_o} \times 100$
38.3	11.13	11.31	- 0.18	-1.6
56.0	12.82	12.34	+ 0.48	3.7
79.6	13.19	9.61	3.58	27.1
77.1	14.64	11.03	3.61	24.7
110.0	13.88	9.91	3.97	28.6
223.8	11.50	5.43	6.07	52.8
300.7	5.43	3.41	2.02	37.2
Totals	22.96		19.55	

the stored damage appeared to have annealed out at 56°K, while the data of Table 8.A. show that only 4.2% had annealed out at this temperature. They interpret these results in either of the following ways:

1) The damage anneals out on warming and then reconstitutes itself rapidly on cooling back to 20°K; or

2) There is a change in the physical properties of plutonium in the temperature region between 20° and 56°K.

We would agree with Olsen & Elliott that their second explanation is more plausible and would suggest that it is the extreme temperature dependence of the additional resistivity which is responsible for the discrepancy. We cannot believe that their first suggestion was meant to be taken seriously.

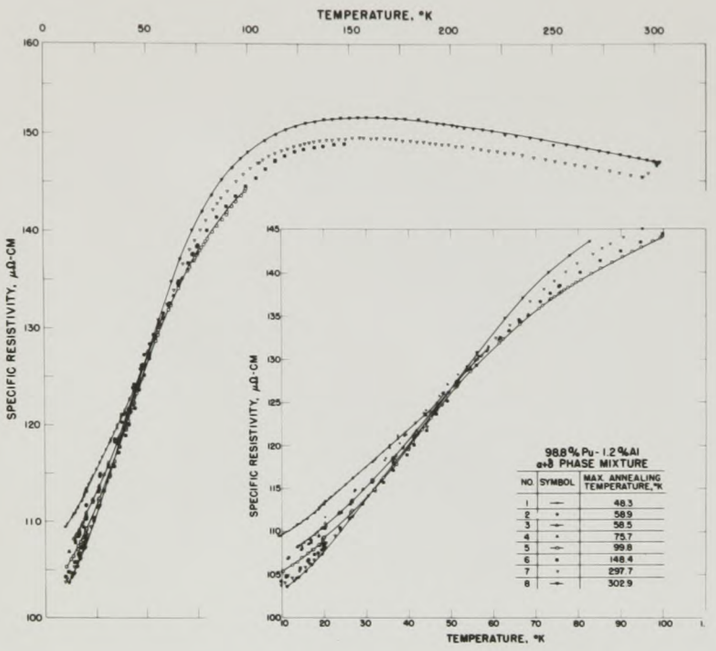

TEMPERATURE, °K
SPECIFIC RESISTIVITY, μΩ-CM
98.8% Pu - 1.2% Al
α+β PHASE MIXTURE
NO. | SYMBOL | MAX. ANNEALING TEMPERATURE, °K
1 48.3
2 58.9
3 58.5
4 75.7
5 99.8
6 148.4
7 297.7
8 302.9

FIG. 8.3

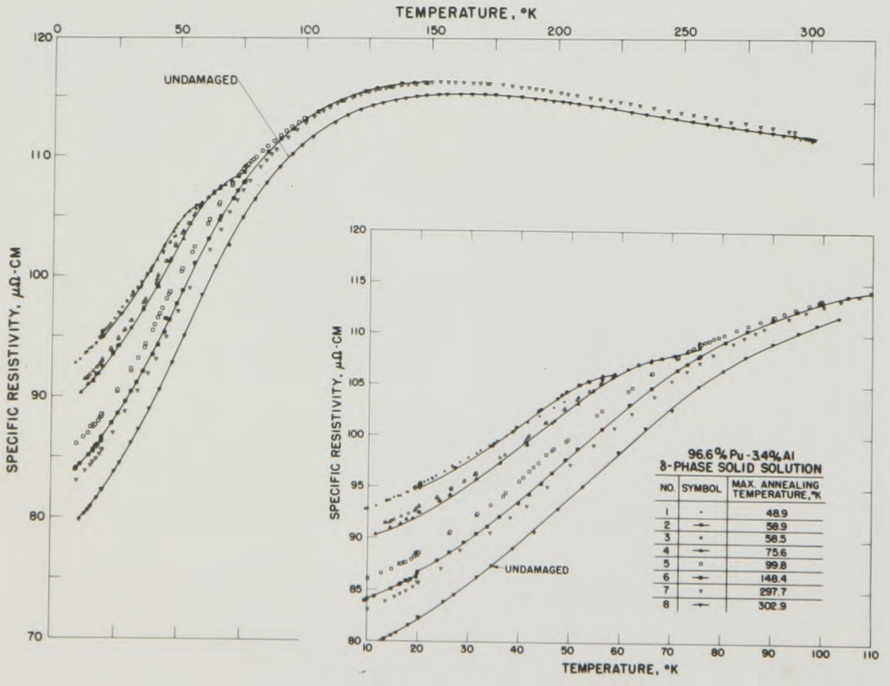

TEMPERATURE, °K
UNDAMAGED
SPECIFIC RESISTIVITY, μΩ-CM
96.6% Pu - 3.4% Al
δ-PHASE SOLID SOLUTION
NO. | SYMBOL | MAX. ANNEALING TEMPERATURE, °K
1 48.9
2 58.9
3 58.5
4 75.6
5 99.8
6 148.4
7 297.7
8 302.9
UNDAMAGED

FIG. 8.4

In their latest paper, Elliott, Olsen and Vineyard (1963), these authors present their results on the low temperature self-irradiation properties of three δ alloys containing 1.2 At.%, 2.5 At.%, and 3.4 At.% Al. respectively. Of these, only the 3.4 At.% Al. specimen is stable at room temperature and below while the 1.2 and 2.5 At.% Al. transforms to α + δ phase mixtures below room temperature. The 1.2 At.% Al. specimen can in many respects be considered as extremely impure α plutonium and provides a useful comparison with the stable 3.4 At.% Al. δ specimen. In Fig. 8.3. the resistivity of the 1.2 At.% Al. specimen is shown as a function of temperature in the undamaged state and during warming to each of a series of higher temperatures. These results closely resemble those obtained by us at various stages during the isothermal anneal of α Pu. 2 which were shown in Fig. 6.3. Below ~ 50°K the resistivity of the 1.2 At.% Al. specimen decreased during annealing, while above ~ 50°K the resistivity increased, although after annealing to room temperature the resistivity was still considerably lower than in the undamaged state.

The effects of self-irradiation on the 3.4 At.% Al. δ specimen, which are shown in Fig. 8.4, present a completely different annealing pattern. At all temperatures the resistivity in the damaged state is greater than in the undamaged state and annealing causes the resistivity to decrease at all temperatures. These results support our own observations that the resistivity of δ plutonium measured at ~ 5°K increases after long periods of self-irradiation to values in excess of the value of the resistivity maximum in the undamaged state. In comparison the ~ 5°K resistivity of α plutonium after long periods of self-irradiation is always less than the value of the resistivity maximum on first cooling.

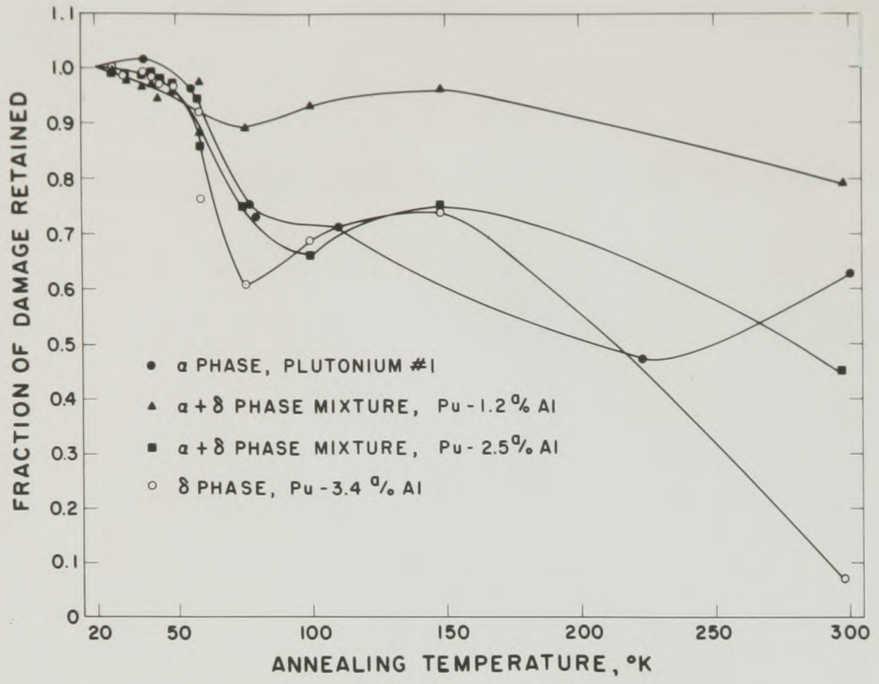


FIG. 8.5

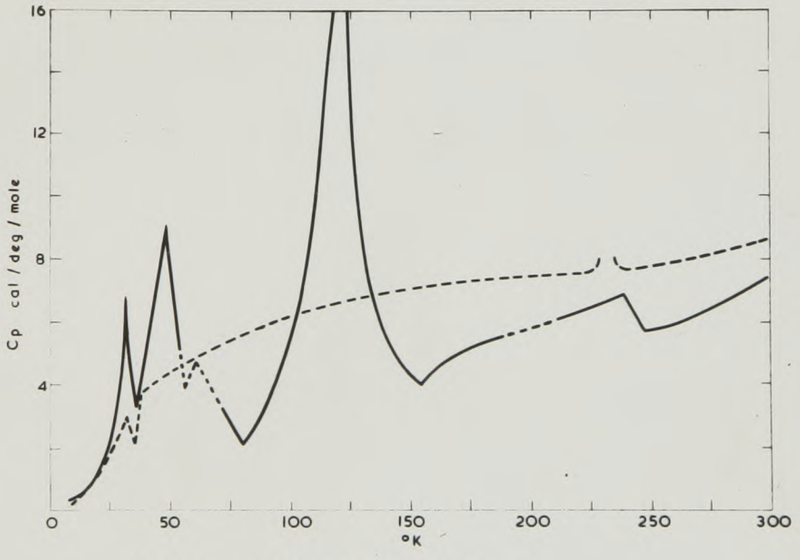


FIG. ■ SPECIFIC HEAT OF PLUTONIUM
(ACCORDING TO SANDENAW, OLSEN, AND GIBNEY)

FIG. 8.6

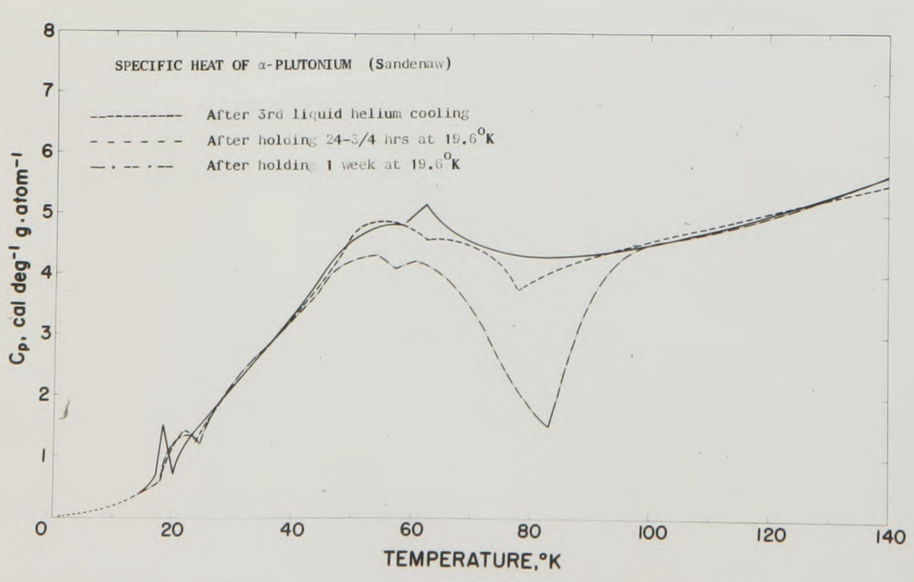


FIG. 8.7

Finally in this section on the electrical resistivity results of Olsen and Elliott, Fig. 8.5. shows the fraction of the damage retained after annealing to the temperature indicated. The fraction of damage retained was obtained by measuring ρ 20°K before and after annealing. It was, however, not stated how quickly the specimens were warmed to the annealing temperature or for how long they were held there. Comparisons between this data and our own isochronal annealing data of Chapter 5 are therefore extremely difficult. If the apparent increases in $(\Delta\rho/\Delta\rho_o)20^\circ K$ after annealing to higher temperatures are genuine and not due to experimental errors, we are no more able to advance a plausible explanation for this retrogressive behaviour than are the authors, Olsen and Elliott.

8.2. Specific Heat Measurements

The first reported measurements of the low temperature specific heat of α plutonium were those of Sandenaw, Olsen and Gibney (1960) and are shown in Fig. 8.6. The reality of the peaks in this figure was however in considerable doubt due to the admitted irreproducibility of the results from run to run. Later results of Sandenaw (1962) which are given in Fig. 8.7. show none of the peaks of Fig. 8.6. except for the one at ~ 60°K. An extremely important effect which is demonstrated in Fig. 8.7. is the release of stored energy in the range 60 - 90°K. The depth of the minimum in the measured specific heat versus temperature curve was found to be dependent on the length of time held at ~ 20°K prior to the commencement of the run. The difference in summed enthalpy at 100°K between a specific heat run on an essentially undamaged specimen and a specific heat run on the same specimen after storage for one week

at ~ 20°K was found to be 62 cal./g.atom. Calculations by Vineyard based on the expected number of Frenkel pairs produced per disintegration in a sample of plutonium stored for one week at low temperatures, predicted the storage of 107 cal./g.atom. Agreement between the theoretical estimate and the measured value was thus quite good. Furthermore the temperature range over which stored energy release occurred, ~60 to ~90°K, corresponds well to the temperature range of our first annealing peak.

Finally, recent results of Loasby, Kay and Taylor (priv. comm.) on the low temperature specific heat of α plutonium quenched to ~ 17°K and then immediately warmed to ~ 100°K, show no anomalies in the specific heat greater than 0.1% in this temperature range. A previous experiment had shown no anomalies in the range ~ 100 to ~ 300°K to the same limit of 0.1%. Thus they found no confirmation of any of the peaks found by Sandenaw for undamaged α plutonium, nor did they find any anomaly which could be attributed to a magnetic ordering phenomenon. By calculating the lattice specific heat for a Debye Θ of 192°K and the dilational term $(Cp - Cv) = \frac{TV\alpha^2}{\chi}$ from the elastic constants reported by Kay & Lindford (1960) and then subtracting these terms from the measured specific heat, they obtain an "Excess Specific Heat" term which must either be due to the electronic specific heat or to an anharmonic lattice term. As this excess specific heat was found to vary linearly with temperature and to extrapolate reasonably well to zero at 0°K, it was assumed that the excess specific heat was due solely to the conduction electrons. For α plutonium this gave γ = 0.05 cal./mole with a consequent density of states N(E) at the Fermi level of 4.5 levels/eV/atom. This compares with

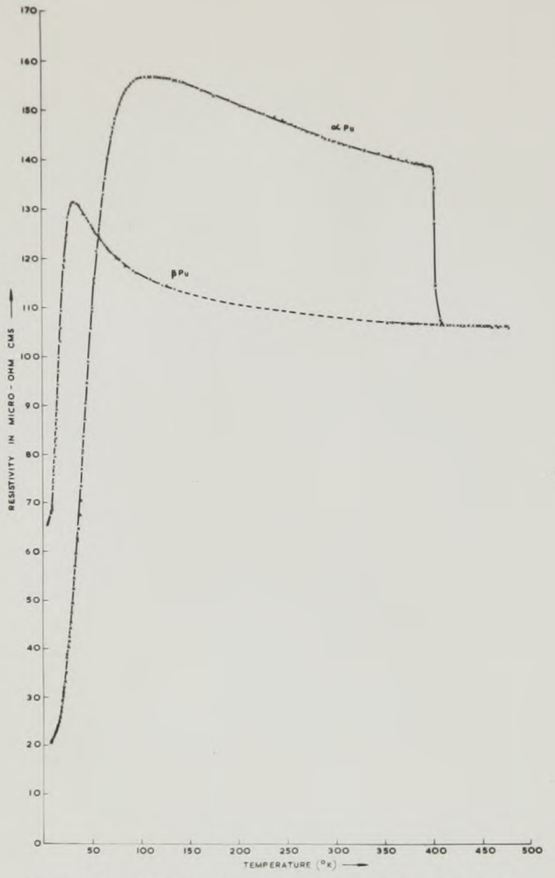


FIG 8 RESISTIVITY - TEMPERATURE VALUES FOR HIGH PURITY PLUTONIUM

FIG. 8.8

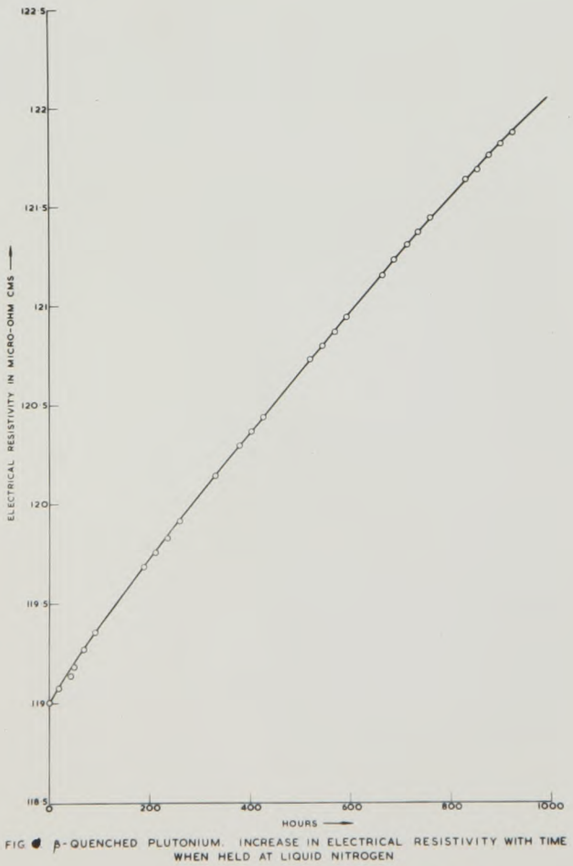


FIG 9 β-QUENCHED PLUTONIUM. INCREASE IN ELECTRICAL RESISTIVITY WITH TIME WHEN HELD AT LIQUID NITROGEN

FIG. 8.9

a value for N(E) of 8.7 obtained from magnetic susceptibility and values of from 10.4 to 18.2 levels/eV/atom obtained by Sandenaw. Even allowing for this rather wide variation, there can be no doubt that there is a high density of states at the Fermi level as required by the theories of Varley, (1956) Lee and Hall, (1959), Rocher, (1962) and Smoluchowski (1962.

8.3. Measurements on beta quenched plutonium

We have already noted in Chapter 1 that Lee and King have perfected a quenching technique by which the β phase of plutonium normally unstable on cooling below $\sim 350^{\circ}K$, has been retained to low temperatures. A preliminary report on this work has been published by them (King and Lee, 1963) from which we have taken Fig. 8.8. It can be seen that β plutonium reaches a much sharper maximum at a lower temperature and of a lower value than does α plutonium. The residual resistivity is also considerably higher than for α plutonium. Their apparatus is not yet capable of holding specimens for long periods at ~ 5 or $\sim 20^{\circ}K$ but Lee & King have carried out a self-irradiation experiment at $\sim 77^{\circ}K$. The electrical resistivity of β plutonium as a function of time held in liquid nitrogen is shown in Fig. 8.9. This data is as yet unpublished and we are grateful to Lee & King for permission to make use of their results. It can be seen that the rate of resistivity increase decreases with holding time. We have made an estimate of the possible value of the resistivity measured at $77^{\circ}K$ as it approaches its asymptote.

If we call this saturation value of $\sim 77^{\circ}K$ resistivity ρ_s and if the resistivity increases according to the exponential law,

$$\rho = \rho_0 + (\rho_s - \rho_0)(1 - e^{-\beta t}) \quad \text{——————} \quad 8.i.$$

it can be shown that this leads to the result

$$\left.\frac{d\rho}{dt}\right|_t \propto (\rho_s - \rho) \quad \text{——————} \quad 8.ii$$

where ρ is the measured resistivity at time t. Then for times $t = o$ and $t = \tau$ we have

$$\frac{\left.\frac{d\rho}{dt}\right|_{t=o}}{\left.\frac{d\rho}{dt}\right|_{t=\tau}} = \frac{\rho_s - \rho_o}{\rho_s - \rho_\tau} \quad \text{——————} \quad 8.iii$$

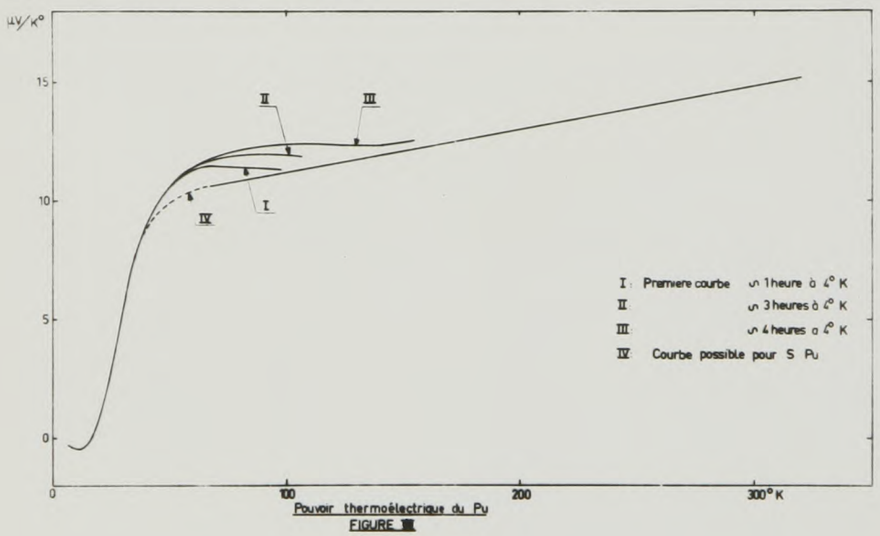
Now from Fig. 8.9. $\rho_o = 119\ \mu\Omega$cm. and $\frac{d\rho}{dt} \simeq 3.8 \times 10^{-3}\ \mu\Omega$cm/hr.

while at $\tau = 980$ hours $\rho = 122\ \mu\Omega$cm and $\frac{d\rho}{dt} \simeq 2.64 \times 10^{-3}\ \mu\Omega$cm/hr.

Substitution in Eqn. 8.iii gives $\frac{3.8}{2.64} = \frac{\rho_s - 119}{\rho_s - 122}$

Solving gives $\rho_s \simeq 129\ \mu\Omega$cm.

This analysis is of necessity crude but does, we hope, give a saturation value of the correct order of magnitude. Should the rate of resistance increase at longer holding periods not follow the same pattern as for short holding periods, the analysis would be completely invalid. If however our value of $\sim 129\ \mu\Omega$cm. is roughly correct, then by reference to Fig. 8.8. it will be seen that the saturation value of $\sim 129\ \mu\Omega$cm. is of a similar magnitude to that of the resistivity maximum of $\sim 132\ \mu\Omega$cm. This would then be extremely similar to the results obtained by us for $\sim 77^{\circ}$K irradiation of α plutonium in which the resistivity measured at $\sim 77^{\circ}$K increased by a value very similar to the value of the resistivity maximum obtained on first cooling. Furthermore the rates of resistivity increase measured at $\sim 77^{\circ}$ during holding at



Pouvoir thermoélectrique du Pu
FIGURE III

FIG.8.10

$\sim 77^{\circ}K$ are similar for α and β plutonium; 1.63×10^{-3} $\mu\Omega$ cm/hr. for α Pu. 9 and 3.8×10^{-3} $\mu\Omega$ cm/hr. for the β plutonium of Lee and King. Further comparisons are rendered difficult by the lack of information about the annealing stages of β plutonium and by the fact that $\sim 77^{\circ}K$ is a higher temperature than that of the resistivity maximum in β plutonium but is a lower temperature than the resistivity maximum in α plutonium.

If the rate of resistivity increase in β plutonium continues to decrease with holding time and saturates at ~ 129 $\mu\Omega$ cm. there will be strong evidence for the belief that the resistivity changes observed are indicative of genuine self-irradiation damage in β plutonium. If however the rate of resistivity increase does not further decrease with holding time, or even starts to increase, it would then appear that the β plutonium is, under the influence of self-irradiation, reverting to α plutonium. If this were the case the $\sim 77^{\circ}K$ resistivity might be expected to saturate at a value more nearly 160 $\mu\Omega$ cm. than 130 $\mu\Omega$ cm.

8.4. Thermo-electric power measurements

The initial measurements of the thermo-electric power of plutonium at low temperatures carried out by Meaden & Lee (1962) were only made down to $\sim 20^{\circ}K$ because at lower temperatures the thermo-electric power of their copper-constanton thermocouples became too small for accurate measurements. Lallement (to be published) has since remeasured the thermo-electric power down to $\sim 5^{\circ}K$ and his results are shown in Fig. 8.10. The most important feature apparent in these results is the effect on the thermo-electric power between ~ 70 and $\sim 150^{\circ}K$ of extremely short self-irradiation periods at $\sim 5^{\circ}K$. No change in the thermo-electric power at $\sim 5^{\circ}K$ was found after up to 12 hours at $\sim 5^{\circ}K$

but after only one hour at ~ 5°K there was a considerable increase in the thermo-electric power between ~ 70 and ~ 150°K. Lallement interprets these results on the basis of a magnetic order-disorder transition at ~ 50°K, as proposed by Rocher (1962). By assuming that a certain amount of local order exists above T_c and that the thermo-electric power of the ordered phase above T_c is greater than that of the disordered phase, he accounts for the observed increase in thermo-electric power above ~ 70°K after irradiation at ~ 5°K. This explanation involves many as yet unproved assumptions, not the least of which is the assumption that there exists a magnetic order-disorder transition at ~ 50°K. The existence of such a transition temperature and of its decrease with pressure is also required to explain the minimum in the expansion coefficient below ~ 50°K reported by Lallement in the same paper. Leaving aside such speculation as to the causes of the observed changes in thermo-electric power after low temperature self-irradiation we should like to comment on the persistence of these changes to temperatures as high as ~ 150°K. We have shown that recovery of the additional resistivity produced by self-irradiation occurs mainly in two stages centred at ~ 80 and ~ 160°K respectively. It would thus appear that the defects which cause the change in thermo-electric power are not removed at the ~ 80°K annealing stage, but persist until the ~ 160°K stage.

8.5. Lattice Expansion Measurements

Although it is possible of little immediate relevance to our consideration of the low temperature self-irradiation behaviour of metallic plutonium, we have included in this section the work of Rand,

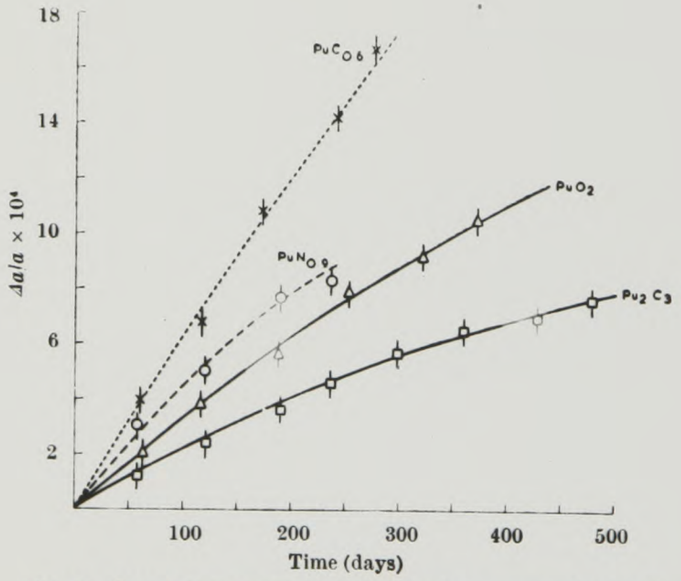


Fig. 8. Lattice expansions of some plutonium compounds stored at ~ 20° C.

FIG. 8.11

Fox and Street (1962) on the lattice expansion of some plutonium compounds during storage at room temperature. The relative lattice expansions, $\frac{\Delta a}{a}$, of these compounds are shown as a function of holding time in Fig. 6.11. It can be seen that there is a tendency to saturation evident for most of the compounds. The authors explain this type of build in on the following assumption: if a recoil atom traverses a region where damage has already occurred no further damage is produced, so that the number of atoms affected by each disintegration is proportional to the number remaining unaffected. Now Y, the fraction of atoms affected is given by: $Y = 1 - e^{-\gamma t}$, γ being constant, and $\frac{\Delta a}{a}$ is assumed to be proportional to Y.

We have also considered the possibility that the observed rate of resistance increase in our plutonium samples is governed by a similar saturation mechanism to that described above. These calculations are given in Appendix IV and will be discussed in the next chapter.

No observations on the change of lattice parameter during holding at low temperature have to our knowledge been made. Indeed very few measurements of low temperature lattice parameters have been made at all; those recently reported by Lallement and Pelenta will be discussed in the next chapter.

CHAPTER 9

Further Comments and Conclusions

In this thesis we have presented our results on the changes in the electrical resistance of plutonium, uranium and neptunium brought about by the storage and annealing of defects produced by self-irradiation at low temperatures. Some of these results have been analysed and discussed in detail, and, although relevant to the thorough understanding of the subject, those analyses may have tended to overshadow the more important results. We shall therefore begin this chapter with a short summary of what are, in our opinion, the most important aspects of our results.

9.1. A Summary of the Experimental Results

9.1.i. Alpha Plutonium

Self irradiation at ~ $5^{\circ}K$ of α plutonium causes the resistivity to increase with time in a manner given approximately by the formula: $\rho = \rho_0 + (\rho_\infty - \rho_0)(1 - e^{-\alpha t})$. In all except the highest purity plutonium samples the rate of resistivity increase is lower when held at ~ $20^{\circ}K$ than at ~ $5^{\circ}K$. This is not, however, due to annealing but to the temperature dependence of the additional resistivity produced by the self-irradiation. Experiments such as those shown in Fig. 3.5. and Fig. 6.6. show that the highly temperature dependent resistivity of α plutonium is rendered almost temperature independent after long periods of self-irradiation at very low temperatures. Thus

the additional resistivity does not obey Matthiessen's law. The resistivity of heavily damaged alpha plutonium is virtually temperature independent up to at least 120°K and possibly higher at a value less than that of the original resistivity maximum. The resistivity measured below ~ 50°K increases during self-irradiation at very low temperatures while the resistivity measured above ~ 50°K decreases. On annealing to ~ 90°K the reverse process occurs and the resistivity measured above ~ 50°K returns virtually to its pre-irradiation value. The resistivity measured below ~ 50°K is not fully annealed in this first stage but anneals partially in a second distinct stage at ~ 160°K and then gradually to room temperature where only a few percent of the original resistivity increase remains unannealed. Analysis shows that at ~ 90°K the anneal follows second order rate Kinetics with an activation energy of about 0.2 eV. In contrast to the decrease in resistivity measured above ~ 50°K as a result of self-irradiation at ~ 5°K, irradiation at ~ 77°K causes a slight increase in the resistivity measured at ~ 77°K as well as a substantial increase in the resistivity measured at ~ 5°K.

9.1.ii. Delta stabilised plutonium

When held at ~ 5°K the resistivity of δ plutonium increases initially at a much slower rate than that found for α plutonium. It does not, however, reach its asymptotic value so quickly as does α plutonium and the value of its asymptotic resistivity is considerably larger than the value of the resistivity maximum in the undamaged state. It is found that specimens of δ plutonium stabilised with different

concentrations of aluminium have different initial rates of resistivity increase and the magnitude of the initial rate of resistance increase can be explained if it is assumed that the saturation value is similar for all aluminium concentrations. Matthiessen's law is still not obeyed, but the deviations are smaller than found for α plutonium. Isochronal studies show that annealing commences at lower temperatures than for α plutonium, that the first stage is enhanced at the expense of the second stage and that after annealing to room temperature a greater percentage of the resistivity increase remains unannealed in δ plutonium than in α plutonium.

9.1.iii. Other results

We have shown that the resistivities of uranium 233 and neptunium 237 specimens increase when the specimens are held at $\sim 5^{\circ}K$. The self heats of these isotopes are considerably lower than that of plutonium, and the rates of resistivity increase are lower than those found for plutonium. The relative rates of resistance increase are described more accurately by the application of Walker's rule than by a simple comparison of the isotopic self heats.

9.2. Possible interpretations of the observed results

9.2.i. We have little doubt that the fundamental mechanism which causes the change in the physical properties of metals exposed to fast particle irradiation is the production of interstitial-vacancy, or Frenkel, pairs. What is not so clear is the exact way in which these basic defects cause the observed changes in the physical properties of the metal under consideration. In particular there is usually no way

of proving whether the defects are produced by a simple cascade process or by one or more of the various types of spike mechanism.

We feel that the saturation effect observed in the electrical resistivity of alpha and delta plutonium may be best explained by assuming that the damage is produced in spikes similar to those found for fission fragment damage. If it can be assumed that the passage of a recoil uranium 235 atom produces so much damage to the lattice in the region through which it has passed that the passage of a second recoil through the same region causes no further damage, saturation is caused by the steady decrease in the amount of material remaining undamaged.

We have calculated the number of atoms affected by each spike for alpha and delta plutonium and these calculations are given in detail in Appendix IV. It is found that the damaged volume produced by one disintegration in alpha plutonium contains approximately 1.6×10^5 atoms. If it can be assumed that the estimate of 1,600 Frenkel pairs per disintegration obtained from cascade theory is approximately valid for the spike mechanism considered, we find that there is a concentration of 1% Frenkel pairs in the damaged volume. It is probable that the passage of a second recoil through this region would increase this concentration of Frenkel pairs but we have assumed that this leads to no further measurable change in the electrical resistivity.

In delta plutonium stabilised by the addition of 4 At.% aluminium it is found that the volume damaged per disintegration contains approximately 5.5×10^4 atoms. If the estimate of 1,600 Frenkel pairs per disintegration is still valid, we find that there is now a 3% concentration of Frenkel pairs in the damaged region. This threefold

increase in the number of Frenkel pairs in the damaged region would appear to be the root cause of the difference in saturation rates observed in alpha and delta stabilised plutonium.

9.2.ii.

We are not in a position to explain our results until we have made some assumptions about the way in which the defects introduced by self-irradiation affect the electrical resistivity of plutonium. In the simplest possible case we could assume that the vacancies and interstitials behave like impurities and add a temperature independent contribution to the resistivity. This model holds quite well for small impurity or defect concentrations in simple metals such as copper. For plutonium, especially for alpha plutonium, this model is not applicable. We have shown that the addition of small amounts of chemical impurities can cause a large increase in the residual resistivity of α plutonium and little change or even a slight decrease in the resistivity at room temperature. As the addition of impurities does not lead to a uniform "classical" increase in the resistance, we should not expect defects introduced by self-irradiation to follow a simple model. Changes in the electrical resistivity of plutonium should, we feel, be considered as a whole and not split up into temperature dependent and temperature independent components.

One model which enables us to take this approach is that of low temperature antiferromagnetism in α plutonium with a Neel temperature between 50 and 60°K. As yet there is no proof that such behaviour exists in plutonium, indeed the lack of anomalies in the magnetic susceptibility and specific heat and the absence of an ordered superlattice

shown by neutron diffraction present considerable difficulties to the acceptance of an antiferromagnetic theory of plutonium. However in all of these critical experiments the conditions were such that the absence of an affirmative result does not automatically disprove the existence of low temperature antiferromagnetism. For example, the neutron diffraction experiments performed at Harwell were only on δ stabilised plutonium and those at Los Alamos were only carried out down to ~ 23°K. Furthermore the Los Alamos workers reported that they saw no changes in the position and intensity of the lines as might have been expected if there is a structural change at ~ 30°K as indicated by the X-ray data recently reported by Lallement and Solente. Similarly the magnetic susceptibility experiments of Weil et al. were performed on very low purity material and cannot be considered as very reliable. Thus, as the existence of low temperature antiferromagnetism in plutonium has not yet been disproved, we consider that it is worth while discussing our results in terms of this model.

Let us consider the results shown in Figs. 3.5., 6.3., and 6.6. on the assumption that α plutonium is antiferromagnetic below ~ 55°K. The observed magnitude of the residual resistivity is then due to a certain percentage of the spins being prevented from ordering by the presence of chemical or physical impurities. On warming the specimen the ordered spins are thermally disordered until at the Neel point at 55°K long range order is completely destroyed. The existence of short range order above T_N is then assumed capable of giving the observed maximum and subsequent decrease in resistivity according to the formula

$$\rho_m = \rho_{m_{T\to\infty}}\left(1 + a\,\frac{T_c}{T} - b\,\frac{T_c}{T}^2 + \text{- - -}\right) \qquad 9.1.$$

by taking into account the spin correlation effects on first and second nearest neighbours.*

If now the specimen is held at ~ 5°K for a considerable period we assume that some of the ordered spins can be disordered by the self-irradiation damage stored in the specimen. We do not consider that self-irradiation directly disorders the spin system but rather that those atoms carrying a localised moments are displaced from their lattice sites into interstitial or grain boundary positions, so destroying the ordered arrangement of spins. On warming the damaged specimen there are now fewer ordered spins to be thermally disordered and in consequence the resistivity increases less rapidly. At ~ 55°K the resistivity has virtually the same value as it had in the undamaged state, that corresponding to the complete absence of long range order. If we now assume that only those spins which were thermally disordered on warming to ~ 55°K can cause local ordering above ~ 55°K, it can be seen that there will be a smaller amount of local order above T_N. The resistivity maximum will thus be reduced in magnitude.

After an extremely long period of self-irradiation at low temperatures, all the long range order will be destroyed and there will be no more spins to be disordered on warming the specimen to T_N. Similarly above T_N no short range order would exist and we would have a virtually temperature independent resistivity above and below T_N at the value of $\rho_{m_p \to \infty}$ in equation 9.i. Any residual temperature dependence

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*We are grateful to Y.A. Rocher (priv. comm.) for this information

of the resistivity would then be due to electron-phonon scattering. The absence of such a residual temperature dependence gives weight to the assumption that such a phonon term is negligibly small for plutonium.

On annealing the reverse process occurs. Once some of the defects have been annealed it becomes possible for a partially ordered arrangement of spins to exist below the transition temperature and the resistivity due to spin disorder scattering decreases. Above T_N local order starts to reappear and the resistivity rises. Eventually after fully annealing at ~ 90°K many of the spins are free to align on cooling below T_N and to produce local order above T_N. Not all of the defects are however removed in the ~ 90°K annealing stage; let us call those which are annealed during the 90°K stage type A defects. Those defects remaining (type B, say) are able to prevent complete ordering below T_N but do not apparently affect the local ordering at temperatures higher than T_N.

To explain the results of holding a sample of alpha plutonium at ~ 77°K we have to assume that only type B defects are stored at ~ 77°K. These cause the resistivity measured at ~ 5°K to rise to about 100 $\mu\Omega$ cm. and the resistivity measured at ~ 77°K to rise to the value of the resistivity maximum. We have thus had to postulate the existence of two different types of defect with the following properties:

Type A Is stored at ~ 5°K and annealed at ~ 80°K. It causes an increase in resistivity measured below ~ 55°K and a decrease in the resistivity measured above ~ 55°K.

Type B Is stored at ~ 5°K and at ~ 77°K and annealed at ~ 160°K and higher temperatures. It causes an increase in the resistivity measured above and below ~ 55°K.

It must also be assumed that the decrease in resistivity above ~ 55°K caused by a type A defect is larger than the increase in resistivity caused by a type B defect.

There is at this stage no justification for trying to identify our type A and B defects with conventional defects such as interstitials or vacancies. It is quite possible that type A may be partially caused by an increase in the number of current carriers or type B by a decrease in number or mobility of current carriers.

Thus it can be seen that it is possible to explain our results on α plutonium by assuming the existence of antiferromagnetism below ~ 55°K. We feel that it is not unreasonable to expect ferro- or antiferromagnetism in the actinide series of metals, especially plutonium, in view of the structural similarities between the actinide and lanthanide series in metals. If antiferromagnetism should exist in alpha plutonium it is most likely to be of the helimagnetic type about the b axis as the monoclinic structure of alpha plutonium would be too complex to support a simpler type of magnetic order.

9.2.iii

Rocher and Friedel (1961) have also proposed an antiferromagnetic model to explain the low temperature properties of delta plutonium. They furthermore explain the anomalous increase in low temperature resistivity of δ stabilised plutonium with increase in aluminium content

(shown in Fig. 1.3.) by assuming that a superexchange mechanism can couple antiferromagnetically two plutonium atoms via an intermediate aluminium atom. If this mechanism does exist in δ stabilised plutonium it is possible that the defects produced by self-irradiation could also behave like additional aluminium atoms and cause a larger increase in the resistivity at low temperatures than at high or intermediate temperatures. Unfortunately the 4 At.% Al. δ specimen which underwent over 8,000 hours self damage at ~ 5°K has not yet been warmed to room temperature and we do not know the temperature dependence of the resistivity in the heavily damaged state. It is probable that it becomes virtually temperature independent, as does alpha plutonium, but it is possible that it might have a negative temperature coefficient of resistance at very low temperatures similar to that found for a Mn.-5% Fe.-5% Cr. alloy by Bellau and Coles (1963).

Our speculation that delta stabilised plutonium could revert to alpha plutonium after long periods of self damage at low temperatures is also without confirmation. Elliott has shown that when a 3.4 At.% plutonium alloy was subjected to a high pressure at room temperature some alpha phase was precipitated that did not revert to delta phase when the pressure was removed. Thus when δ Pu. 4 is eventually warmed to room temperature any alpha phase plutonium which might have been formed during low temperature self-irradiation should be stable and metallographic or X-ray analysis should be able to confirm or refute our speculation.

As the existence of anti-ferromagnetism in alpha plutonium at low temperatures has not yet been proved we shall reconsider some of the alternative explanations put forward to explain the low temperature

properties of plutonium.

9.2.iv.

Smoluchowski (1962) based his explanation of the very low temperature properties of plutonium on a theory originally put forward by Wilson which has never been successfully applied to any metal. Smoluchowski's justification of a low temperature phonon cut off was stated to be the exponential dependence of the low temperature resistivity as the temperature tended to absolute zero. We have demonstrated that this relationship does not hold for alpha plutonium and the validity of his theory must therefore be considered doubtful.

At higher temperatures his explanation of the negative temperature coefficient of resistance as due to interband scattering is similar to that proposed by Chandrasekhar and Hulm for gamma uranium alloys. In isolation it would seem to provide a credible explanation of the observed phenomena. However it does not seem reasonable to use different models to describe the resistivity behaviour above and below ~ 100°K and if the low temperature resistivity drop is not caused by a quantum limitation of the number of phonons available for interband scattering, we should hesitate before applying the interband scattering model to the high temperature resistivity.

Before leaving the subject of the negative temperature coefficient of resistance above the resistivity maximum in alpha plutonium, we should like to reconsider one of the possible consequences of Brodsky's Hall effect results which were discussed briefly in chapter 1. If the change from a negative Hall coefficient at ~ 77°K to a positive coefficient at

room temperature were due to the thermal excitation of electrons into a narrow band leaving holes in the top of the broad band from which the electrons were excited, it is possible that there would be a considerable net increase in either the number or the mobility of the current carriers in that temperature range. If this were so it would be possible to explain the negative temperature coefficient of resistance of α plutonium above $\sim 100^{\circ}K$ on this model. Our observation that the addition of impurities tends to decrease the resistivity in this temperature range would then seem to indicate that the impurity atoms form traps which can be ionised at these temperatures. However it is impossible to see how such a mechanism could explain the sharp low temperature decrease in resistivity of all three phases of plutonium.

2.2.v.

The existence of a low temperature phase transformation in alpha plutonium was first postulated by Sandenaw (1960) to explain an effect in the thermal expansion coefficient and a specific heat peak both of which he found at $\sim 50^{\circ}K$. Recent results of Lallement (to be published) do not confirm the discontinuity in expansion coefficient found by Sandenaw but show that the expansion coefficient gradually changes sign at about this temperature. Other recent X-ray diffraction results of Lallement and Solente (priv. comm.) seem to indicate that there is a change in atomic parameter on cooling below $\sim 30^{\circ}K$. Possible confirmation of this result may be found in the work of Sandenaw and Olsen (1960) which showed a slight offset in the electrical resistivity at $\sim 30^{\circ}K$. However no confirmation for this offset was found by Meaden (thesis 1961)

and none of our results show such an anomaly. Furthermore we have found no indication of hysteresis in the resistivity of any of our specimens which had been quenched from ~ 77°K to ~ 5°K. Such hysteresiis might have been expected if there were a phase transformation at either ~ 50°K or ~ 30°K. If such a phase change should be found to exist at ~ 30°K it would further complicate a situation in which there is already a surfeit of experimental anomalies and a distinct lack of suitable theoretical explanations.

Before leaving the subject of a possible low temperature phase change in alpha plutonium we must mention that there is much evidence to show that there is some form of anomaly in the crystallographic structure of alpha uranium at ~ 43°K. Fisher and McKimin (1961) found that there were anomalies in the elastic moduli near 43°K and conclude that they cannot be interpreted as due to a first order phase change because of the absence of a suitable specific heat anomaly. Berlincourt (1959) found that the Hall coefficient changed sign and Meaden (1961) showed that there was a discontinuity in the electrical resistivity near this temperature. Barrett, Mueller and Nitterman (1963) have shown that there is a minimum in the atomic parameters at ~ 43°K indicated by both X-ray and neutron diffraction. Furthermore they have observed extra reflections in the neutron diffraction pattern at low temperatures and they speculate on the possibility of magnetic ordering at low temperatures.

Finally Jousset and Quere (1963) have shown that the resistivity of a sample of zone refined uranium quenched from ~ 50°K to ~ 5°K has a higher resistivity than that of a sample cooled slowly through this

temperature range. This additional resistivity was found to anneal below ~ 43°K. Specimens quenched from below ~ 43°K to ~ 5°K showed no resistivity increase indicating that the resistivity enhancement must be intimately connected with the other anomalies found at ~ 43°K.

Thus uranium as well as plutonium shows distinct anomalies in its low temperature properties. Furthermore Meaden (thesis 1961) has found that there are two possible anomalies of an unknown nature in the low temperature resistivity of neptunium. It seems possible that such behaviour is a general characteristic of the heavier actinide metals. It is not yet clear whether these anomalies are magnetic in origin but in view of the strong similarities between the lanthanide and actinide series of metals it would seem premature to reject such a possibility at this stage.

9.2.vi.

Over the range ~ 0.2 to ~ 2 Θ_D the resistivity of most non-ferromagnetic metals increases linearly and is given by the formula, ρ = constant + KT, where the value of K depends on the metal considered. Lucasson and Walker (1962) have shown that the resistivity increase, $\Delta\rho_p$, brought about by a 1% concentration of Frenkel pairs in a metal, is proportional to this coefficient K. More generally they formulate the rule that this resistivity increase $\Delta\rho_f$ is equal to the change in resistivity between room temperature and the absolute zero. $\Delta\rho_{(300-0)}$. They also show that the rule is more nearly obeyed for defects produced by electron irradiation than for those produced by neutron irradiation and that agreement is better for heavy than light metals.

Vineyard (quoted by Olsen and Elliott 1962) has shown that

application of Walker's rule to the initial rate of resistivity increase in alpha plutonium leads to an estimate of ~ 1,700 Frenkel pairs produced per α disintegration, which is the same value as that given by standard cascade theory. Our calculations on the saturation of the resistivity increase observed in alpha plutonium indicate that a 1% concentration of Frenkel pairs increases the resistivity measured at ~ 5°K from ~ 47 to ~ 141 $\mu\Omega$cm. which is very similar to the original undamaged ~ 300°K resistivity of ~ 150 $\mu\Omega$cm. Similarly our calculations on the saturation of the resistivity increase in a 4 At.% Al. delta stabilised plutonium sample, indicate that a 3% concentration of Frenkel pairs is required to cause saturation. Simple application of Walker's rule to this problem would give a 2.2% concentration of Frenkel pairs. Furthermore our experiments on the self-irradiation of uranium 233 and neptunium 237 show that the observed rates of resistance increase are in agreement with those predicted by the use of Walker's rule.

It would thus appear that, although originally formulated to explain the effect of electron irradiation induced defects in simple metals, Walker's rule may also be applied with considerable success to the defects produced by self-irradiation in such complex metals as plutonium.

What is not at this stage clear is the reason why alpha plutonium requires a 1% concentration of Frenkel pairs to cause saturation in the resistivity increase, while our 4 At.% Al. delta alloy requires a 3% concentration. Furthermore it would be extremely interesting to see if there would be any saturation of the rate of resistance increase if large concentrations of defects were produced in simple metals such as copper.

In short is there an upper limit to the resistivity increase which can be caused by putting defects into a simple metal or is the saturation of the resistivity increase which we have observed in alpha and delta plutonium a direct consequence of the existence of low temperature antiferromagnetism in plutonium?

9.3. Conclusions

The results presented in this thesis have been explained where possible in terms of conventional theories of irradiation effects in metals. It has however been found necessary to adopt a more comprehensive approach to the problem in order to explain the effects observed in alpha and delta stabilised plutonium. We have attempted to interpret our results in terms of current theories of the low temperature properties of plutonium and we find that they may be best explained by assuming that alpha plutonium is antiferromagnetic below ~ 55°K. As yet there is no definite evidence to prove or disprove this suggestion but we feel that there must be some logical explanation for the many anomalies found at or near ~ 55°K. If irradiation damage experiments were performed on a known antiferromagnetic such as alpha manganese, and if these experiments showed the same effects as those observed by us on plutonium, the case for low temperature antiferromagnetism in alpha plutonium would be considerably strengthened.

If on the other hand it is shown conclusively that alpha plutonium is not antiferromagnetic at low temperatures, any alternative explanation will have to explain successfully our observed results, especially the increase in resistivity below ~ 55°K and decrease in resistivity above

~ 55°K, after irradiation at ~ 5°K.

Apart from the need to carry out irradiation experiments on known antiferromagnetics, further work is desirable on the self-irradiation properties of delta plutonium alloys. If possible they should be performed on a range of aluminium compositions and also on delta plutonium stabilised with other elements such as cerium. In view of the long periods which would be necessary to produce substantial defect concentrations, we do not consider that further self-irradiation experiments on neptunium 237 would be worthwhile. Irradiation experiments with an external source of particles should, however, be undertaken on uranium and neptunium to see whether there is any saturation of the additional resistivity caused by the storage of defects at low temperatures. Neutron irradiation experiments on uranium with a high proportion of the 235 isotope should prove particularly rewarding because of the large amounts of fission fragment damage which can be introduced in this manner.

Finally when protoactinium becomes available in suitable metallic form, low temperature self-irradiation experiments should be performed on this element. The self heat of protoactinium is similar to that of plutonium and it is therefore to be expected that defects will be formed at approximately the same rate as in plutonium. As protoactinium occurs early in the actinide series of elements, it is reasonable to expect that its low temperature resistivity will have a temperature dependence more like that of thorium than that of plutonium, and it would be of considerable interest to see if there is any saturation of the self-irradiation induced resistivity increase in this metal.

APPENDIX I

a/ Details of Specimens used for self-irradiation experiments

Identity	Colour	S.N.	Mass gm	Phase/Comp.	Purity	Density gm/cc	Isot.	Length cm	Diameter cm	Form	Form Fact. cm
Pu.1.	Red	4460	1.8771	α	mod.	19.61	A	19	2.52	mach.	4.75×10^{-2}
Pu.2.	Yellow	4233	0.4799	α	mod.	19.65	B	37	0.885	extr.	2.41×10^{-3}
Pu.3.	Green	4501	2.1100	α	mod.	-	A	22	2.50	mach.	2.86×10^{-2}
Pu.4.	Blue	4616	0.179	4 At % Al δ	-	-	A	3.5	1.26×10^{-1}	sheet	1.47×10^{-3}
Pu.5.	Wht/Red	4939	2.2935	α	mod.	19.45	A	32	1.70	extr.	5.87×10^{-3}
Pu.6.	Grn/Brn.	4940	1.9830	α	mod.	19.27	B	49	1.645	extr.	6.03×10^{-3}
Pu.7.	Red/Yel.	5198	1.6306	α	low	19.43	D	41	1.65	extr.	6.62×10^{-3}
Pu.8.	Red	5301	1.7196	α	high	19.60	C	42.7	1.625	extr.	6.30×10^{-3}
Pu.9.	Black	5302	1.8177	α	mod.	19.32	B	44.5	1.66	extr.	5.955×10^{-3}
Pu.10.	Grn/Yel.	5655	1.568	α	mod.	-	B	38.2	1.65	extr.	6.75×10^{-3}
Pu.11.	Red/Blk.	5665	0.5851	α	high	-	F	42	0.966	extr.	2.23×10^{-3}
Pu.12.	White	5820	0.2525	8 At % Al δ	-	15.48	A	31	0.828	extr.	2.26×10^{-3}
U.233.	Blk/Yel.	39650	0.0145	α	-	18.38	-	55	.2	mach.	4.75×10^{-3}
Nep.	Red/Brn.	5858	0.3339	α	-	20.02	-	38.7	0.741	extr.	1.38×10^{-3}

APPENDIX I

b/ Self heats of α-active Isotopes. (neglecting β and γ absorption)

	Pa.231	U.233	Np.237	Pu.238	Pu.239	Pu.240	Pu.241	Am.241
Self Heat mw/gm	1.2086	0.2745	0.01973	570.38	1.9013_6	7.025_4	(13.45)	106.60

c/ Isotopic analyses of "Experimental Purposes" Plutonium stocks

	STOCK					
Isotope(%)	A	B	C	D	E	F
Np.237	.019	.0091	.0095	.0090	.0098	-
U.238	.0539	.0063	.0095	.078	.0254	.01
Pu.238	.004	.03	.006	.030	.003	
Pu.239	96.628	90.686	95.393	90.359	97.924	93.52
Pu.240	3.150	8.552	4.254	8.692_5	1.978	5.95
Pu.241	.109	.323	.1655	.535	.0333	.49
Am.241	.026	.33	.083	.224	.0156	.009
Pu.242	.0096	.0725	.0095	.0727	.0098	.02
Self Heat mw/gm	2.123_8	2.093_7	2.457_9	2.810_5	2.039_1	2.27

a/ Experimental values of resistivity as a function of temperature for α Pu.8 (high purity) in the undamaged and damaged states

UNDAMAGED		After 357 hours at 5°K		After 767 hours at 5°K	
T°K	ρ ($\mu\Omega$ cm)	T°K	ρ ($\mu\Omega$ cm)	T°K	ρ ($\mu\Omega$ cm)
0	28.6	0	51.9	4.2	70.939
4.2	29.158	4.2	52.319	5.9	71.244
7.05	29.435	5.8	52.460	6.3	71.381
7.55	29.573	5.95	52.482	6.6	71.531
8.75	30.174	6.3	52.550	7.5	71.843
9.35	30.389	6.7	52.663	8.25	72.180
10.1	30.849	7.05	52.917	8.90	72.559
11.5	31.816	8.05	53.331	9.60	72.915
13.1	33.289	9.1	53.894	11.30	74.195
15.6	36.542	10.25	54.557	12.2	75.163
18.85	42.482	12.45	56.460	14.25	77.463
21.25	47.907	16.1	61.473	16.6	81.022
22.85	52.322	19.3	67.611	17.6	82.668
24.9	58.956	21.3	72.056	20.45	87.814
27.65	67.710	23.55	77.928	21.9	91.283
29.25	72.947	25.20	82.668	23.4	94.851
32.25	83.003	27.35	88.998	24.95	98.487
37.0	98.921	29.70	95.530	25.9	101.029
39.0	107.350	31.75	101.193	28.95	108.140
44.3	120.342	33.7	106.615	30.5	111.640
47.5	127.745	35.55	111.510	31.75	114.421
51.1	135.129			33.3	117.704
56.1	143.112			34.08	119.424
77.3	159.857			34.41	120.193

APPENDIX IIa continued

After 1200 hours at 5°K		After 1918 hours at 5°K		After 3024 hours at 5°K	
T°K	ρ (μΩ cm)	T°K	ρ (μΩ cm)	T°K	ρ (μΩ cm)
0	89.28	0	110.9	0	127.98
4.2	89.471	4.2	(110.751)	4.2	128.014
6.1	89.762	6.1	111.262	6.0	128.225
8.1	90.498	6.6	111.402	6.4	128.287
8.55	90.613	7.4	111.569	7.4	128.414
9.7	91.193	8.25	111.833	8.3	128.560
10.7	91.915	9.35	112.285	9.0	128.755
11.85	92.777	9.95	112.445	10.0	128.997
13.5	94.249	10.85	112.902	11.0	129.388
15.2	96.395	12.15	113.677	13.85	130.569
18.0	100.310	14.9	115.887	16.25	131.793
20.75	104.982	18.5	119.443	20.0	133.926
23.6	110.338	20.75	121.997	23.15	135.954
27.75	118.253	23.45	125.451	26.65	138.215
31.25	124.270	25.8	128.439	29.9	140.030
33.85	128.703	28.18	131.146	32.2	141.236
34.9	130.223	31.08	134.391	35.0	142.558
		33.75	137.215		
		35.9	139.243		

APPENDIX II

b/ Experimental values of resistivity as a function of temperature for α Pu.9 (medium purity) in the undamaged and damaged states

UNDAMAGED		After 337 hours at 5°K		After 647 hours at 5°K	
T°K	ρ (μΩ cm)	T°K	ρ (μΩ cm)	T°K	ρ (μΩ cm)
0	50.38	0	71.22	0	86.26
4.2	50.662	4.2	71.624	4.2	86.557
6.2	51.150	6.8	72.008	7.5	87.242
6.5	51.269	7.5	72.358	7.7	87.324
11.3	54.086	8.05	72.651	8.1	87.440
13.5	56.185	8.90	73.074	8.4	87.022
14.75	57.997	9.45	73.461	8.95	87.991
15.55	59.193	10.3	74.197	9.55	88.327
18.2	63.525	11.0	74.622	10.4	88.878
20.4	67.920	12.46	75.902	(11.35)	89.856
21.2	69.828	15.6	79.571	13.3	91.321
23.3	74.521	19.6	86.056	14.55	92.544
24.75	78.070	21.9	90.159	15.85	94.160
28.55	87.695	24.45	95.247	17.4	96.105
30.85	93.875	26.7	100.145	19.0	98.371
32.85	98.863	29.15	105.007	20.15	100.065
36.4	107.711	30.75	108.351	21.7	102.542
38.65	112.326	33.2	113.264	23.65	105.791
42.0	119.785	34.8	116.301	24.55	107.205
46.0	126.990	36.5	119.353	25.65	109.143
51.15	135.506	37.9	121.884	27.3	111.761
		39.7	125.100	28.8	114.544
		After 647 hours cont'd.		29.5	115.715
		33.5	121.955	30.5	117.307
		35.1	124.239	31.8	119.401

APPENDIX III

The Evaluation of Activation Energies by the method of Meechan & Brinkman

The recovery of certain physical property changes in solids during annealing often obeys an equation of the form

$$dp/dt = F(p,q_1 \cdots q_n)e^{-E/kT} \quad \text{——— 1}$$

where p is the measured property, t is the time, T is the absolute temperature, k is Boltzmann's constant, E is the activation energy and the q_is are variables independent of t and T depending on the past history of the specimen.

Equation 1 can be integrated as follows:

$$\lambda\,(p,q_i) = \int_{p_0}^{p} \frac{dp}{F(p,q_i)} = \int_0^t e^{-E/kT}\,dt = \Theta \quad \text{——— 2}$$

where Θ is referred to as the temperature compensated time.

For identical specimens, with the same history prior to annealing, the q_is need not be considered, then for such specimens the inverse function of Eqn. 2 is

$$p = p(\Theta) \quad \text{——— 3}$$

Consider two specimens with identical histories. The first is isochronally annealed, the temperature intervals need not be equal, and p is measured at the end of each pulse after quenching to a reference temperature at the temperature coefficient of p is not negligible. Let T_i be the temperature, which must be kept constant, during the i^{th} pulse, p_i the measured value of p after the i^{th} pulse, Θ_i the corresponding value of Θ according to Eqn. 3 and t_i the total time elapsed at the end of the i^{th} pulse.

For a given pulse one can write:

$$\Delta\Theta_i \equiv \Theta_i - \Theta_{i-1} = \Delta t\, e^{-E/kT} \quad \text{——— 4}$$

if the recovery is all characterised by a single activation energy E

according to Eqn. 1

$$\text{Now } \Delta t = t_i - t_{i-1} = \text{constant} \quad \text{——— 5}$$

as the time intervals are equal.

Equation 4 can be rewritten:

$$\ln \Delta \Theta_i = c' - E/kT_i \quad \text{——— 6}$$

where $c' = \ln \Delta t$

The second specimen is annealed at a single temperature and the recovery of ρ measured as a function of the annealing time. Let Ta be the temperature of the isothermal anneal and let τ be the annealing time. The experimental ρ vs. τ curve obtained for the second specimen can then be used to determine the Θ values to be used in Eqn. 6 for the first specimen.

From 2 it can be seen that

$$\tau = \Theta e^{E/kTa} \quad \text{——— 7}$$

Let τ_i denote the value of τ corresponding to Θ_i. Then

$$\Delta\tau_i = \tau_i - \tau_{i-1} = \Delta \Theta_i \; e^{E/kTa} \quad \text{—— 8}$$

or

$$\ln \Delta\tau_i = \ln \Delta\Theta_i + c'' \quad \text{——— 9}$$

where $c'' = E/kTa$

On substitution in Eqn. 6 one gets

$$\ln \Delta\tau_i = c - E/kT_i \quad \text{——— 10}$$

where $c = c' + c''$

For the general case described above it is necessary that the two specimens have the same initial defect concentrations. However there are cases such as when the chemical rate equation,

$$d\rho/dt = -\nu \rho^n e^{-E/kT} \quad \text{——— 11}$$

is obeyed, where identical histories are not necessary. In the case

where 11 is valid, the isothermal curves of two specimens with different initial defect concentrations will be identical, with the exception of a displacement of the origin, $\tau = 0$. Hence while the measured τ values will differ for two such specimens (by the amount by which the origin is displaced) the $\Delta\tau$ values will be the same, and Eqn. 11 will still be valid.

From the p vs. τ curve obtained with the second specimen one can determine τ_i corresponding to each p_i measured on the first specimen. The $\Delta\tau_i$ for each successive pulse, corresponding to the appropriate T_i, can thus be determined and by plotting ln $\Delta\tau_i$ vs. $1/T_i$, a straight line then gives E according to Eqn. 10. If recovery from annealing in a given temperature interval has more than one value of E, then the ln $\Delta\tau_i$ vs. $1/T$ plot will exhibit straight line segments in each interval in which only a single value of E is effective, but will give a curve in overlapping regions where there are two or more values of E.

APPENDIX IV

Calculations on the Saturation of the Additional Resistivity produced by Self-irradiation Damage in Alpha and Delta Stabilised Plutonium

If it can be assumed that the passage of a recoil U.235 atom through a region that has already been damaged, produces no further damage, saturation effects of type found by us for α and δ plutonium can be simply explained. The fraction of atoms affected is given by $Y = 1 - e^{-\alpha t}$

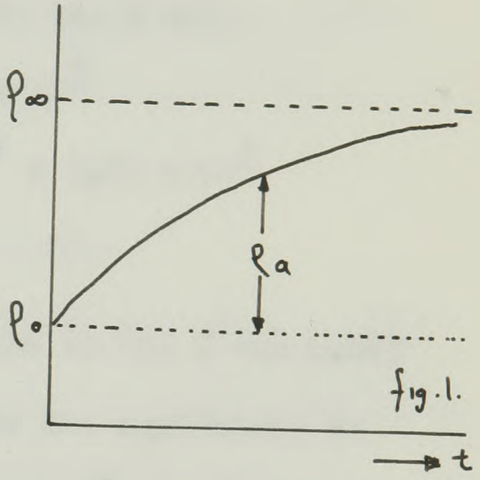


fig.1.

and if it can be assumed that $Y = \frac{\rho_a}{\rho_\infty - \rho_0}$ (the symbols are shown in Fig. 1) we have

$$\rho_a = (\rho_\infty - \rho_0)(1 - e^{-\alpha t})$$

IV a) Now for α Pu.2, $\rho_\infty - \rho_0 = 141 - 47 = 94\ \mu\Omega$ cm. If we assume that for the first 1%, i.e. 0.94 $\mu\Omega$ cm., of this increase every recoil atom passed through an undamaged region of the lattice, we can evaluate the number of atoms affected by each recoil atom, as we know the initial rate at which the resistivity increased; 0.053 $\mu\Omega$ cm/hr.

Pure Pu.239 has a half life of 24,360 years and consequently a fraction of atoms decaying per second $\lambda = 9.016 \times 10^{-13}$. In fact α Pu.2 had the Isotopic composition given in Table I, Appendix Ic and a resultant self heat of 2.039 mW/gm. compared with a value of 1.901$_4$ mW/gm for pure Pu. 239. Thus to obtain a more realistic value of the decay constant λ we have used the relation

$$\frac{\lambda \text{eff. Pu.2}}{\text{self heat Pu.2}} = \frac{\lambda \text{Pu.239}}{\text{self heat Pu.239}}$$

This gives a value λ eff. $= 9.667 \times 10^{-13}$

The number of atoms per cc. of Pu. 239 is N_o x density/Atomic Weight

$$= \frac{6.023 \times 10^{23} \times 19.6}{239} = 4.94 \times 10^{22} \text{ atoms/cc.}$$

Hence number of atoms decaying per hour per cc. in Pu. 2 was

$$= \lambda \text{ eff.} \times \text{no. atoms/cc.} \times 3.60 \times 10^{3}$$

$$= 9.667 \times 10^{-13} \times 4.94 \times 10^{22} \times 3.60 \times 10^{3}$$

$$= 1.719 \times 10^{14} \text{ atoms/hour/cc.}$$

Now the initial rate of resistivity increase in Pu. 2 was 0.053 $\mu\Omega$ cm/hr. and 1% of the total resistivity increase was equivalent to 0.94 $\mu\Omega$ cm., then the number of hours taken to reach 1% of the total resistivity increase $= \frac{0.94}{0.053} = 17.7_3$ hours

and the number of disintegrations taking place per cc. in this time

$$= 17.7_3 \times 1.719 \times 10^{14}$$

$$= 3.05 \times 10^{15} \text{ disintegrations/cc.}$$

Thus 3.05×10^{15} disintegrations have damaged 1% of 1 cc. Therefore the volume damaged by one disintegration is

$$\frac{10^{-2}}{3.05 \times 10^{15}} \text{ cc.} = 3.28 \times 10^{-18} \text{ cc.}$$

Now 1 A° $= 10^{-8}$ cm. and 1 cu.A° $= 10^{-24}$ cc.

Therefore volume damaged per disintegration $= 3.28 \times 10^{6}$ cu.A°

This volume is equivalent to that occupied by a sphere of radius $\sim 92 A^{\circ}$. Vineyard (quoted by Olsen & Elliott (1962)) has given values of 500 A° for the range of an α particle and 60 A° for the recoil U.235 atom in plutonium. Using the value of 60 A° for the range of the U. 235 recoil we could alternatively find that the volume of 3.28×10^{6} cu. A° would

be occupied by a cylinder 60 A° long and ~ 265 A° in diameter. We do not however intend to speculate on the exact shape or form of the damaged regions.

We found earlier that the volume damaged by the products of one disintegration was 3.28×10^{-18} cc. and also that plutonium has 4.94×10^{22} atoms per cc. Thus the number of atoms in the damaged region is

$3.28 \times 10^{-18} \times 4.94 \times 10^{22}$

$= \underline{1.62 \times 10^{5} \text{ atoms in the damaged volume}}$

Now Vineyard (quoted by Olsen & Elliott (1962)) has given a value of 1,700 for the number of Frenkel pairs produced per α - disintegration. Kinchin and Pease (1955) and D'Eye and Roberts (1957) have given a value of ~ 1,500 Frenkel pairs/disintegration. All of these estimates have been obtained by the use of cascade theory which may or may not be valid for the case which we are considering. However in the absence of any alternative estimates we shall assume an intermediate value of ~ 1,600 Frenkel pairs/dis^{n}. Then as the damaged region contains 1.62×10^{5} atoms

$$\frac{\text{No. of F. pairs/dis}^{n}.}{\text{No. of atoms in damaged region}} = \frac{1.6 \times 10^{3}}{1.6_{2} \times 10^{5}} \approx \frac{1}{100} = 1\%$$

Thus we have a 1% concentration of Frenkel pairs in the damaged region of α Pu.

IV b) We shall now consider the saturation effect in δ Pu. 4 in the same way. In this case $\rho_{\infty} \simeq 153\ \mu\Omega$cm. and $\rho_{0} = 90\ \mu\Omega$cm. hence $\rho_{\infty} - \rho_{0} = 63\ \mu\Omega$cm. and the first 1% of the resistivity increase corresponds to $0.63\ \mu\Omega$cm. The initial rate of resistivity increase in δ Pu. 4 was $0.012\ \mu\Omega$cm/hr.

The self heat of δ Pu. 4 2.02_5 mW/gm. is so similar to the value of 2.039 used for Pu. 2 that we shall not recalculate the value of λ eff. The number of atoms /cc. is less in δ Pu. than in α Pu. and is given by N_o x density/Atomic weight.

$$= \frac{6.023 \times 10^{23} \times 15.6}{239} = \underline{3.94 \times 10^{22} \text{ atoms/cc.}}$$

Thus number of atoms decaying per cc. per hour in Pu. 4 was

$$= 9.667 \times 10^{-13} \times 3.94 \times 10^{22} \times 3.60 \times 10^{3}$$

$$= \underline{1.371 \times 10^{14} \text{ atoms/hour/cc.}}$$

Now the initial rate of resistivity increase in Pu. 4 was 0.012 $\mu\Omega$ cm/hr. and 1% of the total resistivity increase was equivalent to 0.63 $\mu\Omega$ cm., then the number of hours taken to reach 1% of the total resistivity increase

$$= 0.63/0.012 = \underline{52.5 \text{ hours}}$$

and the number of disintegrations taking place in this time per cc.

$$= 52.5 \times 1.371 \times 10^{14} = \underline{7.20 \times 10^{15} \text{ dis}^{ns}./\text{cc.}}$$

Therefore volume damaged per disintegration $= \frac{10^{-2}}{720 \times 10^{15}}$

$$= \underline{1.39 \times 10^{-18} \text{ cc.}} = \underline{1.39 \times 10^{6} \text{ cu.A}^{\circ}}$$

This volume is equivalent to that occupied by a sphere of radius $\sim 69.3 A^{\circ}$. Once again as the number of atoms/cc. in δ Pu. - 3.94×10^{22}, and the volume damaged per disintegration is 1.39×10^{-18} cc., the number of atoms in the damaged region = $3.94 \times 10^{22} \times 1.39 \times 10^{-18}$

$$= \underline{5.48 \times 10^{4} \text{ atoms in the damaged volume}}$$

Finally if the estimate of 1,600 Frenkel pairs/disintegration is also valid for δ plutonium then

$$\frac{\text{No. of F. pairs/dis}^{n}.}{\text{No. of atoms in damaged region}} = \frac{1.6 \times 10^{3}}{5.48 \times 10^{4}} = \underline{2.92\%}$$

Thus it would appear that the damaged region in δ Pu. (stabilised with 4 At.% Aluminium) has almost 3 times the concentration of Frenkel pairs contained by the damaged region in α Pu.

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