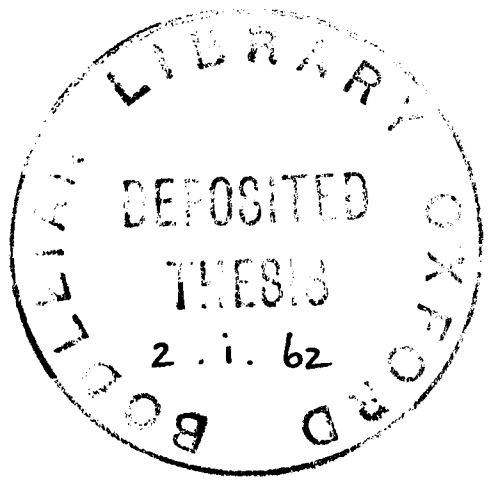
LOW TEMPERATURE PROPERTIES OF TRANSURANIC AND OTHER HEAVY METALS.

A study of the electrical resistivity and thermoelectric power of thorium, uranium, neptunium and plutonium.

A thesis submitted for the degree of Doctor of Philosophy in the University of Oxford.



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ABSTRACT.

The electrical resistivity and thermoelectric power of four members of the actinide series of elements have been measured below room temperature. They include the artificially made, transuranic elements neptunium and plutonium, which are extremely toxic and for which special apparatus had to be designed. Neptunium is a very rare metal and only a small quantity of rather low purity material was available, but the remaining elements were able to be obtained in a high state of purity.

The importance of these metals lies in their nuclear properties, and the employment of alloys of uranium and plutonium as nuclear fuels is now well-established. Under reactor operating conditions, fuel elements are subjected to bombardment from a variety of radiations of differing intensity, to cyclic changes of temperature and resulting thermoelastic stresses. A knowledge of the properties of the materials used in the preparation of the fuel elements, especially at elevated temperatures, is naturally of vital importance, and this accounts for the present pace of research on the subject. While low temperatures themselves are of little interest for the reactor technologist, they provide the physicist with a

powerful tool in his basic research. For, with decreasing temperature, the effects of thermal vibrations are lessened and the properties being studied often yield much further useful information. Low temperature research has its own experimental problems, of course, and the techniques employed are often highly specialised.

With regard to plutonium, no work below 77°K on <u>any</u> of its properties had been carried out in Britain before the present research was started (1957), although since then work has also commenced at A.W.R.E., Aldermaston and at Grenoble. But at Los Alamos some low temperature research was apparently already in progress.

The problems involved in the safe handling of plutonium (and neptunium) are well-known. These metals are extremely dangerous to work with, and great care must be taken to ensure that they do not contaminate the open laboratory. Indeed, the danger level is such that the total body-burden is limited to 0.6 microgram of plutonium, while the airborne limit is set at 2.10^{-12} microcuries per cc. (i.e., 10^{-11} microgram per cc). The difficulties associated with the handling of plutonium metal arise chiefly from its readiness to oxidise at the surface into a non-adherent powder of very small particle size. This leads to a rapid build-up of α-active dust in

the surrounding atmosphere, and, if a particle should become deposited in the body, severe local biological damage would result. Plutonium is therefore normally handled only in glove-boxes, and our cryostat had consequently to be designed to work in conjunction with a glove-box. The problems raised by this are discussed in this thesis, together with the effects caused by the very high self-heating of plutonium. Another method of working with radioactive specimens, in which they are sealed in cylindrical containers, is also described.

The resistances of the actinide metals investigated were found to be high, especially those of neptunium and plutonium, while the thermoelectric powers displayed complicated temperature relationships.

The temperature dependence of the resistance of α-Pu was very abnormal, being characterised by a negative temperature coefficient above 105°K and a sharp fall in resistance below this temperature. Some Pu rich δ-Pu-Al alloys also showed the same phenomenon. An explanation in terms of spin-disorder effects seems quite reasonable, and it is suggested that both α- and δ-Pu may be anti-ferromagnetic.

The resistance-temperature curves of uranium and

neptunium are also unusual in that the temperature coefficients decrease monotonically with rising temperature. Possible reasons for this have been discussed, including that by which Mott accounted for the high temperature resistance of some transition metals. Jones has recently discussed this again more generally, and Chandrasekhar and Hulm have extended it to account for the negative temperature coefficients of b.c.c. uranium alloys. The band structure of the actinide metals is satisfactorily described in terms of a two-band model, in which a broad, low density of states conduction band is overlapped by a narrow, high density of states band. It is assumed that in uranium, neptunium and plutonium the Fermi level lies within this narrow band, but that in thorium the Fermi level has a lower energy than the bottom of this band. The properties of thorium show it to be less abnormal than the succeeding actinides, resembling the transition metals rather than the rare earths.

Uranium was found to display anomalies in both the electrical resistivity and the thermoelectric power at about 40°K. This is close to the temperature at which Berlincourt observed anomalous changes in the Hall coefficient, and may possibly be due to a phase change. Anomalies at 155 and 273°K in one of the neptunium

specimens are also discussed at length, and shown to be due to a ferromagnetic impurity.

A table has been included as an appendix which simplifies the evaluation of characteristic temperatures when comparing experimental resistance data with the Gruneisen-Bloch formula.

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INTRODUCTION.

The work set out in this thesis deals with the electrical resistivity and thermoelectric power of four members of the actinide series of elements below room temperature. These are thorium (atomic number 90), uranium (92), neptunium (93) and plutonium (94). Of the others, protoactinium (91) could not be made available for us in metallic form, while actinium (89) and americium (95) were not obtainable in sufficient quantities.

All of these metals are well-known for their high radioactivity, and most of them are extremely dangerous on account of it. Only thorium and uranium, in fact, are safe to handle in the open laboratory. Plutonium is indeed the most poisonous substance known to man. The hazard involved arises not so much from the strength of the alpha-emission (the alpha-particle range in air is only 3.7 cm.), but rather from its readiness to oxidise quickly into a non-adherent oxide consisting of exceedingly fine particles. This can lead to a rapid build-up of alpha-active dust in the surrounding atmosphere and, as the total body-burden is set at the very low level of 0.6 microgm., operations have to be conducted inside a glove-box. The associated handling difficulties greatly complicate the experimental problem, and it was mainly on

this account that the transport properties chosen for investigation were two of the more straightforward ones from the experimental point of view.

Also, another feature of plutonium which is often of considerable importance when studying its physical properties, is its exceptionally high self-heating. The half-life of commonly available plutonium is ~24,300 years with respect to alpha-disintegration, and the associated self-heating ~2 milliwatts per gm. This results in a 50 gm. mass of metal (i.e., $2\frac{1}{2}$ cc.) being some 10°C or more warmer than its surroundings if these are solely gaseous.

A cryostat suitable for use with these radioactive metals was therefore designed and built, and this is described in Chapter 2 together with full experimental details. This is followed by a full presentation of the results in Chapters 3 and 4. Some discussion of immediately relevant questions is held in these chapters as the data are presented, but the main discussion awaits Chapter 5. Firstly, however, Chapter 1 deals in a general manner with the theoretical state of the electrical resistance of metals.

CHAPTER 1.

The Theory of the Electrical Resistance of Metals.

A full account of the theory of metallic conduction will not be attempted here. Rather, the purpose of this chapter is to indicate the development of the principles and fundamentals that now form the basis of the modern theory of conduction in metals. A rigorous mathematical account of the theory of metals has been given by Wilson (1953), while perhaps the best review of electrical and thermal conductivity is that of Jones (1956).

The chapter will begin with a survey of the early free electron and quantum theories of metallic conduction, and this will be followed by discussions of the problem of the resistance due to thermal scattering at both high and low temperatures. On account of the considerable mathematical difficulties involved, present theories are restricted quantitatively solely to the monovalent metals and then only for normal or high temperatures ($T > \Theta$). At low temperatures the position is still less satisfactory and an analytical solution of the problem in even a qualitative manner has not yet been made. Bloch himself, however, in one of his earlier papers, obtained an

approximate solution, and the so-called Gruneisen-Bloch equation will next be discussed. We will then mention the effect of impurity scattering on the electrical conductivity, and discuss to what extent the more complicated resistances of the multivalent metals can be explained in terms of our present ideas.

Finally, we will deal with the present state of the theory of the thermoelectric effect.

1.1. Free Electron Theories.

The concept of a free electron gas as a basis for the theory of metallic conduction was introduced and developed by Drude (1900) and Lorentz (1905). They conceived the valency electrons as being detached from their atoms and able to move about quite freely, behaving as a perfect gas.

The assumptions of a Maxwell distribution of velocities and of the existence of a time of relaxation then require a solution of the Boltzmann transport equation

$$\frac{\partial f}{\partial t} + \dot{\underline{k}} \nabla_k f + \underline{v} \nabla_r f = \left(\frac{\partial f}{\partial t}\right)_{coll} \qquad \ldots(1)$$

in a very much simplified form, viz:

$$\frac{-e\mathcal{E}}{m} \frac{\partial f}{\partial u} + u\frac{\partial f}{\partial n} = -\frac{f-f_o}{\tau} \qquad \ldots(2)$$

since $\frac{\partial f}{\partial t} = 0$ in the steady state. All the symbols have their conventional meanings as used by Wilson. The usefulness of the idea of a time of relaxation lies in the fact that it simplifies the solution of transport problems and provides the results in a form in which they can be applied to actual metals. It is said to exist if the distribution function f, after removal of the external fields, relaxes exponentially to the equilibrium value f_o when left to the action of the scattering processes alone. Thus

$$\frac{\partial}{\partial t}(f-f_o) = -\frac{f-f_o}{\tau} .$$

The solution of (2) is in fact the well-known formula for the conductivity

$$\sigma = \frac{Ne^2\tau}{m} \qquad \ldots(3)$$

This equation actually gives the correct order of magnitude for σ of, say, silver at room temp., but unfortunately the wrong temperature dependence. For if 2τ is taken as l/u where l, the mean free path, should be of the order of the interatomic distance at room temperature and therefore roughly temperature independent, $\sigma \propto \frac{1}{\sqrt{T}}$ instead of $\frac{1}{T}$, unless l increases considerably at lower temperatures. Indeed l would have to become infinite at the absolute zero in order to explain the vanishing of the thermal resistance there. This was difficult to

understand classically.

Nevertheless, the theory was able to account for the Weidemann-Franz law (constancy of ratio K:σ for all metals at constant temperature), and also gave the constant of proportionality with fair accuracy. This success is somewhat surprising in view of some of the assumptions made, but was clearly due to the underlying correctness of the free electron concept. Also of great importance is the fact that their idea of a mean free path for collisions is retained today in a modified form, while their neglect of electron-electron interactions we now know is largely justified (Jones, 1956).

1.2. Sommerfeld's Theory.

The main difficulty with the classical approach was that it predicted unescapably an additional $\frac{3}{2}Nk$ per unit volume to the heat capacity of the metal from the electrons themselves. This was a consequence of the use of Maxwell-Boltzmann statistics. The actual very small value of the electronic heat capacity remained unexplained until, with the introduction of quantum mechanics, Sommerfeld (1928) was able to apply Fermi-Dirac statistics to the electrons in a metal. He ignored the field acting on a conduction electron due to the ions and to the other

electrons, and found that as before σ was given by eqn.(3). The low specific heat of the electrons was, he found, due to only a small fraction of the electrons being energetically available for conduction (those with energies within kT of E_{max}) and because $E_{max} \gg kT$. Unfortunately, he was still unable to indicate how τ and its temperature dependence could be evaluated.

This was done however by Houston (1928) and Bloch (1928) who investigated the way in which electrons interact with the ions of the crystal lattice.

1.3. General Modern Approach.

Bloch imagined electrons as moving in an electrostatic field having the periodicity of the lattice, so that in a perfect lattice at the absolute zero the mean free path of an electron would be infinite, i.e., the resistance is zero. Scattering will then be caused by anything which upsets the perfect periodicity of the lattice potential, thus giving rise to a finite mean free path. Such scattering may be caused by:

(1) thermal vibrations of the ions of the lattice. Such motion should decrease with decreasing temperature and become very small at the absolute zero. Resistance due to this cause is commonly termed the ideal resistance (see sections 1.4 - 1.5).

(ii) imperfections in the crystal lattice. These may be foreign atoms in solid solution or actual defects of the lattice such as dislocations, grain boundaries or vacancies. Such contributions to the scattering should not be affected appreciably by the temperature, and should account for the residual resistance at the absolute zero (section 1.6).

There can also be other effects present contributing to the scattering - for example in a magnetic metal an atomic arrangement of spins, or the random distribution of atoms in alloys.

Firstly, we deal with the ideal resistance.

1.4. Resistance due to Thermal Scattering.

The usual approach to the problem of calculating the ideal resistance is based on determining the probability of a electron making a transition from one given state to another. The total transition probability for the whole metal is then calculated and this gives us the relaxation time. Simple substitution in eqn.(3) then gives the ideal conductivity at once. The manner in which the various treatments differ lies in the different assumptions that are made concerning the coupling between the electrons and the lattice. As indicated previously, the mathematical difficulties are such that in all quantitative analyses it

has been necessary to simplify the problem by assuming that the energy of an electron in a state $\underline{k}$ depends on $\underline{k}$ only. i.e., the Fermi surface is spherical. This condition of course is nearly satisfied only in the monovalent metals.

In Mott and Jones' calculation (see Jones 1956) the probability that an electron is scattered in a single atomic cell is determined by assuming that effects due to the displacement of the atom can be neglected outside its own cell. The contributions to the scattering from each cell are then summed to obtain the total scattering probability and thence the current. They thus employed an Einstein model, as in Einstein's theory of the specific heats, which is roughly valid only so long as $T > \Theta$ It was, however, simpler than the Debye model which was also used, in which lattice vibrations are treated collectively and are analysed into sound waves. The latter model applies for $T < \Theta$ as well as for $T > \Theta$. In this, the scattering matrix for transitions from a state represented by the wave vector $\underline{k}$ to another state represented by $\underline{k}'$ was found to include the factor $\frac{|\underline{k}-\underline{k}'|}{q}$ where q is the magnitude of a wave vector $\underline{q}$ in reciprocal space. Transitions for which $\underline{k}-\underline{k}'+\underline{q} = 0$ are known as normal processes, while those for which $\underline{k}-\underline{k}'+\underline{q} \neq 0$

are called Umklapp processes. It was found on this model that Umklapp processes accounted for three quarters of the total scattering at high temperatures. Unfortunately, their appearance greatly complicated the mathematics and made further restricting and simplifying assumptions necessary. Umklapp processes however do not occur at low temperatures in the idealised monovalent metals that we are considering.

At normal or high temperatures the Einstein and Debye models were found to lead to approximately the same value for τ and hence also σ. Agreement with the observed conductivity for sodium was moreover quite good, allowing for the rather wide limits of uncertainty in some of the constants. The main advantages of Mott and Jones' methods lie in their relative simplicity and that they yield formulae which are convenient for comparison with experiment.

Perhaps the most satisfactory calculation of the interaction constant available at present is still that of Bardeen (1937). In his approach the scattering matrix was determined by a self-consistent calculation based upon first-order perturbation theory. The agreement attained with the observed conductivity is excellent, but Jones puts forward the criticism that Bardeen nevertheless rather

underestimated the effect of Umklapp scattering. The rôle played by Umklapp processes in other transport phenomena besides electrical conductivity is now more fully appreciated, for it is realised that their partial or whole neglect in the past largely accounts for the shortcomings of present day theory, but the mathematics still appears to be as intractable as ever.

1.5. Thermal Scattering at Low Temperatures.

In the above methods it was possible to make use of the conception of a relaxation time. At low temperatures ($T \ll \Theta$) where the quantisation of the lattice waves makes itself evident, no relaxation time can be specified, so that in order to solve Boltzmann's equation approximate methods must be resorted to.

Bloch himself (1929) gave an approximate solution for the electrical conductivity obtaining an equation which in the low temperature limit gave the resistivity as being proportional to T^5. Gruneisen (1933) went further and suggested that the equation obtained by Bloch might also be applicable at intermediate temperatures since it becomes linear in T at high temperatures. This equation, known as the Gruneisen-Bloch relation, is

$$\rho_i = \frac{C}{\Theta_R}\left(\frac{T}{\Theta_R}\right)^5 \int^{\Theta_R/T} \frac{z^5\,dz}{(e^z-1)(1-e^{-z})} \qquad \ldots(4)$$

where $Z = \frac{\Theta_R}{T}$

It is found that, when C and Θ_R are suitably chosen, this expression represents the experimental results on a number of metals quite closely.

This success is very pleasing when it is remembered that the theory on which equation (4) is based is restricted to isotropic energy surfaces and isotropic scattering of the electrons, besides employing a Debye vibrational spectrum (thus ignoring dispersion of the phonon velocities). It should be noted however that Θ occurs in the formula at a high power and since it is essentially an arbitrary parameter, all one is really doing is curve-fitting. That the Gruneisen-Bloch relation gives a good description of the resistance of a variety of metals is nevertheless true, but significant departures do become evident at the lowest temperatures in the small-angle scattering region. A close look in fact reveals that even in the monovalent elements deviations are such that it is no longer possible to specify Θ_R uniquely (with the sole exception of sodium). Indeed, Θ_R is commonly represented as a function of T in order to illustrate departure from the Gruneisen-Bloch law. At sufficiently low temperatures ρ_i, it is true, does become proportional to T^5 in the monovalent metals

and also in some divalent metals; but in the transition metals the index of T varies between 3 and 5 and in some it is even as low as 2. As we shall see later (Chapter 3) for the actinide metals it is much nearer to 3.

Summing up, then, we find that the modern electron theory of metals gives a reasonably good account of the observed electrical conductivity. There is still a lot to be desired at low temperatures however, especially in the multivalent metals. This is mainly because owing to the rapid temperature variation of the number of phonons with energy, transport properties at low temperatures are particularly sensitive to exact details of the scattering mechanism. A more adequate treatment of Umklapp processes, not only at normal or high temperatures, but also at low temperatures, is clearly necessary. Their inclusion at low temperatures by Ziman (1954) at once gave improved agreement with experiment for both the electrical and thermal conductivities of sodium. Moreover, Bailyn and Brooks (1956) discovered that Umklapp processes dominate the scattering down to the lowest temperatures at which the ideal resistivity can be measured ($\sim 1^{\circ}K$) (which discovery, by the way, resolved Peierls paradox (1932) regarding the thermal equilibrium of phonons at low temperatures). To improve the theory it will also be

necessary to use a more accurate vibrational spectrum than Debye's, and to take into account deviations of the Fermi surface from a sphere.

1.6. Resistance due to Impurity Scattering.

The residual resistance of metals, as mentioned before in section 1.3, arises from the scattering of conduction electrons by impurities in solid solution or other imperfections in the lattice. This scattering is, to a fair approximation at least, independent of the temperature, and the statement that the total resistivity is given by the addition of the impurity and ideal resistivities is known as Matthiessen's rule.

Now a time of relaxation always exists for impurity scattering, since the collisions involved are effectively elastic. This is because the mass of the "irregularity" is so much larger than that of the electron that negligible energy is transferred. If then a time of relaxation also exists for the thermal scattering as at high temperatures, then Matthiessen's rule can be shown to follow immediately. Some departure however might be expected at low temperatures where no τ for the ideal resistivity exists, and deviations have indeed been found (e.g., Gruneisen (1933)). But any deviations are generally very small so that, at least in

most (pure) metals, the assumption of Matthiessen's rule involves no important errors. We have therefore freely made use of the rule in obtaining ideal resistivities for the logarithmic plots of ρ_i against temperature (Chapter 3).

1.7. The Transition Metals.

We have already stressed the difficulties encountered in attempting to provide even a qualitative description of metals other than monovalent ones. This is on account of the extreme complexity of the Fermi surfaces of multivalent metals which overlap two or more Brillouin zones. The use of a two-zone theory has however enabled certain qualitative features of divalent and some other metals such as bismuth to be deduced - at least at high temperatures where a relaxation time can be specified.

The resistivities of the transition metals too, which are very much larger than those of the monovalent metals, have been explained in an approximate fashion on a two-band picture (Mott, 1936), the chief difference being an allowance for inter-zone transitions. The reason for this is because the high resistivities are related to the possession by the transition metals of partially filled d-shells, into which by reason of their

high density of states, there is a large probability of scattering of the (mainly s-) conduction electrons. Further discussion of this important topic will be left until Chapter 5 (section 5.1) when the band structure of the actinide metals, with which there are many features in common, is considered.

We must now draw attention to yet another scattering mechanism which plays an important part in the resistivities of those transition metals and rare earth metals which are ferromagnetic or antiferromagnetic. This is the so-called spin-disorder resistivity which is strongly temperature dependent at temperatures below the Curie or Néel point and almost, if not completely, temperature independent above. The spin-disorder effects (of which an excellent account has been given by Coles (1958)) arise as a result of exchange interactions between the conduction electrons and certain "magnetic" electrons localised on particular atoms, the energy of an interaction depending on the relative orientations of the spins of the electrons involved. The additional resistive component is therefore constant above the Curie or Néel point when the spins are totally disordered, and zero when (or rather if) all the localised spins are

aligned parallel. This kind of behaviour is very clearly seen in α-Mn which is antiferromagnetic, and it also appears in α-Pu (section 3.5) though in this metal the existence of antiferromagnetism has yet to be proved. A full discussion on this subject is left until Chapter 5 (section 5.5.2). We will merely say here that the measured resistance of such metals at the very lowest temperatures ($\sim 1^{\circ}K$) cannot in general be taken as the impurity resistance (section 1.6) since the presence of even minute amounts of specific impurities in solid solution are effective in hindering complete spin alignment, thus giving an appreciable spin-disorder resistivity term.

1.8. The Thermoelectric Effect.

This aspect of transport theory is unfortunately still very imprecisely understood. The main difficulty is that compared with the electrical conductivity, the thermoelectric power is a second-order effect. However, much encouraging progress has been made in the last ten years or so.

Firstly, standard theory (Mott and Jones (1936), Wilson (1953)) leads us to the following equation for the thermoelectric power

$$S = \frac{\pi^2 k^2}{3e}\left(\frac{1}{\sigma}\frac{\partial\sigma}{\partial E}\right)_{\varepsilon=\zeta} T \qquad \ldots(5)$$

This is the so-called diffusion thermoelectric power, and the equation should be valid for all metals. The subscript ζ means the derivative is evaluated at the Fermi surface. $\sigma(E)$, the conductivity function is given by

$$\sigma(E) = \frac{2e^2}{h^2}\int \left(\frac{\partial E}{\partial k_x}\right)^2 \tau(\underline{k})\,\frac{dS}{|\mathrm{grad}_k\, E|}. \qquad \ldots(5a)$$

Alternatively equation (5) can be written

$$S = \frac{\pi^2 k^2}{3e}\left(\frac{\partial}{\partial E}\log \sum_s N_s \tau_s V_s^2\right)_{\varepsilon=\zeta} T \qquad \ldots(6)$$

since the density of states $N(E) = \frac{1}{8\pi^3}\int \frac{dS}{|\mathrm{grad}_k\, E|}$ and the summation is taken over the various separate bands.

For free electrons, where $N(E) \propto E^{1/2}$ and $\tau \propto E^{3/2}$, and considering merely a single band, (6) becomes

$$S = \frac{\pi^2 k^2}{3e\zeta} T \left(\frac{3}{2} + \frac{\partial \log \tau}{\partial \log E}\right)$$

$$= \frac{\pi^2 k^2}{e\zeta} T \qquad \ldots(7)$$

Using instead $2\tau = \frac{l}{v}$, (6) for free electrons becomes

$$S = \frac{\pi^2 k^2 T}{3e\zeta}\left(1 + \frac{\partial \log l}{\partial \log E}\right).$$

Now at low temperatures where the mean free path is determined mainly by impurities, Wilson (1953) assumed l was independent of E (and T), so that

$$S = \frac{\pi^2 k^2 T}{3e\zeta} \qquad \ldots(8)$$

Thus if e is a negative quantity, S is also negative and proportional to T, but if the current is carried mainly by holes in an otherwise full band, e is positive and so is S.

Equation (7) is indeed in <u>qualitative</u> agreement with experiment on quite a number of metals at room temperature, but it breaks down completely at lower temperatures and equation (8) (which is the low temperature form of (7)) is in fact quite inapplicable for the great majority of metals. The thermoelectric power is clearly very sensitive to the precise form of the Fermi surface, for changes in the sign of S occur at a few degrees above absolute zero even in the alkali metals, but the theory as it stood ten or fifteen years ago was quite unable to account for this. Furthermore, whilst Wilson's treatment indicated that S should be affected but little by impurities, the experimental evidence was that at very low temperatures even small amounts of impurity (< 0.01 a/o in some cases) could alter S completely both in sign and occasionally by

as much as a factor of 100 in magnitude (vide the thermoelectric power of copper in section 4.1). This is in strong contrast to the electrical resistance where to a fair approximation the effect of impurities is simply to add a temperature independent component to the resistance.

An advance was made however when Gurevich (1945,1946) drew attention to the significant contribution that "phonon drag" could make. In the usual transport theory it is assumed that the equilibrium of the phonons is unaffected by the electric and thermal currents. This is not exactly so though, particularly at low temperatures, for it is found that the thermal current carried by the phonons can profoundly modify the electric and thermal currents carried by the electrons. This effect is known as the phonon drag. Whereas the corrections to the electrical and thermal conductivities are very small, the contribution to S from phonon drag effects is often very large and, furthermore, can be of either sign (Bailyn, 1958).

Bailyn, in fact, found that in the monovalent metals the Umklapp processes involved in electron-phonon collisions almost always yielded a positive contribution to S, whilst normal non-Umklapp processes gave a negative

contribution. The agreement with experiment that he achieved (for the alkalis), though not exact, is certainly very impressive, when it is realised that he had to balance, as it were, two large components of opposite sign.

The future, then, at least as far as the alkalis are concerned, is very hopeful once the mathematical problems can be overcome. With the polyvalent metals on the other hand, the problem is vastly more difficult, owing to their extremely complicated Fermi surfaces which must play a major part in determining the magnitude and sign of the thermoelectric power.

CHAPTER 2.

The Apparatus and Experimental Procedure*

2.1. Problems Involved when Studying the Transuranic Elements

The design of the cryostat was dictated principally by the fact that experiments on the radioactive transuranic elements were to be carried out. As already pointed out in the introduction, owing to the extreme toxicity of these metals, experiments must normally be carried out in a glove-box. The problem was thus to design and construct a cryostat which could be operated in association with a glove-box, and which took into account the high self-heating of plutonium. Because of the general difficulties and restrictions inherent in the use of a glove-box, it was clearly desirable that the operational side of the cryostat should be kept as simple as possible. Accordingly, it was decided to limit investigations in the first instance to the measurement of properties such as electrical resistance, where adiabatic conditions are not essential - as they are, for example, in calorimetric or thermal conductivity experiments - for then readings can easily be taken while

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* Part of the subject matter of this Chapter has been published as a paper by Meaden and Lee in Cryogenics, 1, 33 (1960).

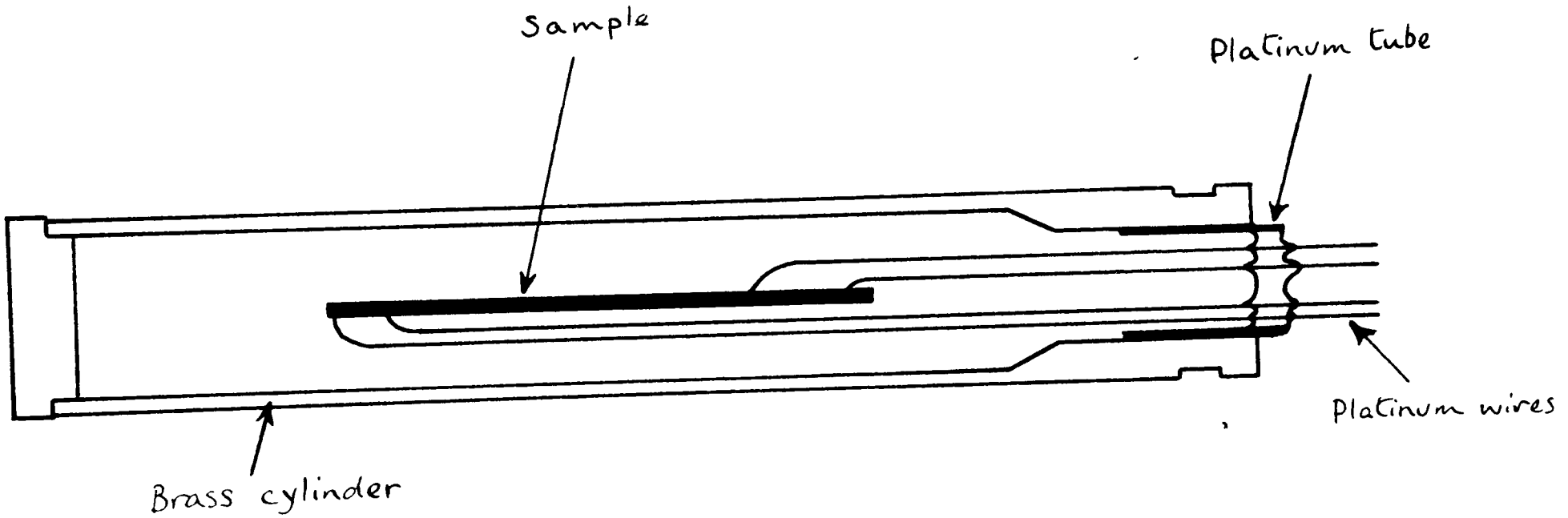


FIG. 2.1 Active Specimen Sealed in a Capsule

(glass capillaries not indicated)

the system is slowly warming or cooling. In addition, the cryostat had to be of such a shape that magnetic experiments could be performed with it at a later date. This cryostat is fully described in section 2.3.

While this cryogenic glove-box was under construction, however, and before it came into full operational use on "active" specimens, an alternative method of experimenting on active specimens was tried, and this is described in the next section.

2.2. The Sealed Capsule Method.

The method involves the sealing of the radioactive samples in small containers and then subsequently making use of a conventional cryostat. Unfortunately, severe limitations are at once imposed on the variety of experiments that are possible by this means. Specimens can easily be canned, for example, for use in magnetic susceptibility or heat capacity experiments where no leads to the specimens themselves are required; but it is less straightforward when one has to provide for the attachment of leads. Nevertheless, several electrical resistivity experiments on canned samples of both Np and Pu rods were performed successfully, and the manner in which the "canning" was done will now be described briefly.

2.2.1. Each container was cylindrical in shape and made

of brass. The overall length was 8 cm., diameter 12 mm. and wall thickness 1 mm. (see fig. 2.1). A platinum-glass seal made from a 1 cm. length of 6 mm diameter platinum tubing had four platinum wires passing through it. These wires were enclosed for most of their lengths in glass capillaries, which increased their strength and eliminated the possibility of shorts onto the container*. The wires were then spot-welded onto a specimen, which was in the form of a rod about 4 cm. in length and 2 mm. in diameter (the spot-welding technique is described in section 2.5.3). The container was then filled with helium gas at normal glove-box pressure, and the platinum-glass seal soft-soldered into its neck. Since the exteriors of the capsule and seal had been coated with shellac before admittance to the glove-box, contamination was later removed by dissolving away the shellac with acetone in a fume-cupboard.

2.2.2. These capsules were found to be perfectly safe and reliable, and most of them made over half a dozen descents to liquid helium temperatures. By this means early resistance-temperature curves on Pu were obtained using the cryogenic glove-box before it was made "active". However, the most important benefit gained from sealing up specimens

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* Earlier capsules had had thin mica sheets on their insides, but such insulation was now rendered unnecessary.

in this way was that two samples of Pu and one of Np were able to be taken to the Clarendon Laboratory, and electrical resistivity measurements made inside a cryostat in which temperatures of 0.75°K were obtainable*. This cryostat had a high speed diffusion pump (1500 litres per sec.) incorporated in the main pumping line and the pressure over the boiling liquid helium could be reduced to a value corresponding to 0.75°K. The temperature below 1.2°K was determined by means of a magnetic thermometer. The results obtained in this investigation are presented in sections 3.4.1. and 3.5.1.

The major drawback to working with radioactive specimens in this manner is soon found if one of the spot-welded contacts becomes loose, as can so easily happen on cooling to low temperatures. The repair of the weld is then a very lengthy job occupying several hours, since it can only be carried out once the specimen in its container has been returned to a glove-box.

Furthermore, in the case of Pu, there is some uncertainty regarding its precise temperature due to its self-heating. This matters most at the lower end of the temperature scale and, for this reason, thick platinum wires were chosen. Even so, the temperature difference

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* The cryostat was very kindly made available by G. Davey.

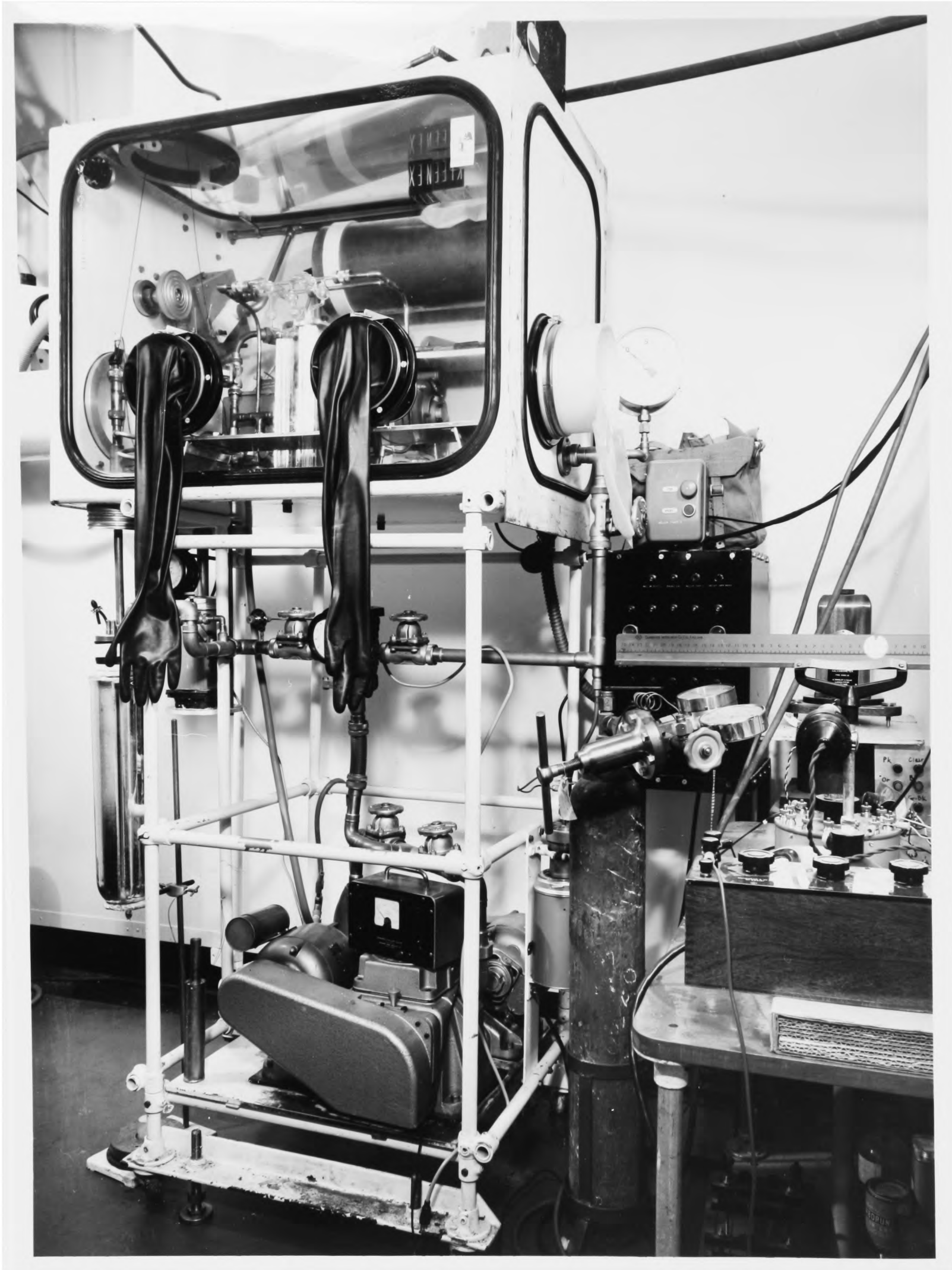


FIG. 2.2

between the specimen and the helium bath was probably as large as 0.05°K.

In the cryogenic glove-box described below, this problem of temperature measurement does not arise, as it is arranged that the specimens are in intimate contact with the liquid helium itself.

2.3. The Cryogenic Glove-Box.

The cryogenic glove-box was the result of combining together the cryostat and the glove-box. The two were indeed almost inseperable, since the main tube of the cryostat was essentially an extension of the glove-box downwards from its floor, being therefore an integral part of the box. But before the design of the cryostat is discussed and a description of its construction and operation given, we must first deal with the principal features of the glove-box itself.

2.3.1. The Glove-Box.

The glove-box was basically a normal one of the free-standing type as widely used at A.E.R.E. for research purposes (figs. 2.2, 2.3). It was of standard dimensions, measuring 39 in. × 29 in. × 24 in. deep, and had perspex panels in the front face and in the roof. Both of these panels were held in place with rubber mouldings in the same



FIG. 2.3

way as are the windscreens of many cars. The two neoprene rubber gloves, set in the front face of the box, were 26 in. in length and 0.030 to 0.040 in. thick through the palm; and the gauntlet of each glove was drawn up to a 1/4 in. diameter bead, in order to enable the glove to be secured to a grooved snout by means of a ring clamp.

Articles of diameter less than $7\frac{1}{2}$ in. were passed into the box through a transfer port over which there was a P.V.C. bag. To effect entry, the article was placed in a pocket in the bag, which was made by pushing the end of the bag inwards, and was then closed by heat-sealing. The bag was then extended into the box and the pocket opened on the box side using scissors. Removal from the box was effected by placing the article in the bottom of the bag, heat-sealing and then cutting along the seal.

In common with most other A.E.R.E. glove-boxes, our box had pure argon for its atmosphere, the purpose being to reduce oxidation of the Pu samples and to prevent the Pu, which in finely divided form is pyrophoric, from catching fire. The box atmosphere was always maintained at a slightly negative pressure relative to the laboratory (about -1 in. static water gauge) to ensure that any leaks were into the box and not out from it. At the same time, this reduced pressure eased glove operation.

Ordinary maintenance to box equipment could be done straightforwardly enough using gloves, but, if repair or replacement of parts that were too large for transferrence through the bag-ports had been necessary, then the box would have been removed to the pressurised-suit (Frog-suit) enclosure. Here it could have been attached by a special flange on one of its faces to an access panel in the wall of the frog-suit area. Access to the interior of the box by a frog-suited man could then have been obtained by removing this face against the access panel. This would have been necessary, for instance, if the rotary pump had had to be replaced.

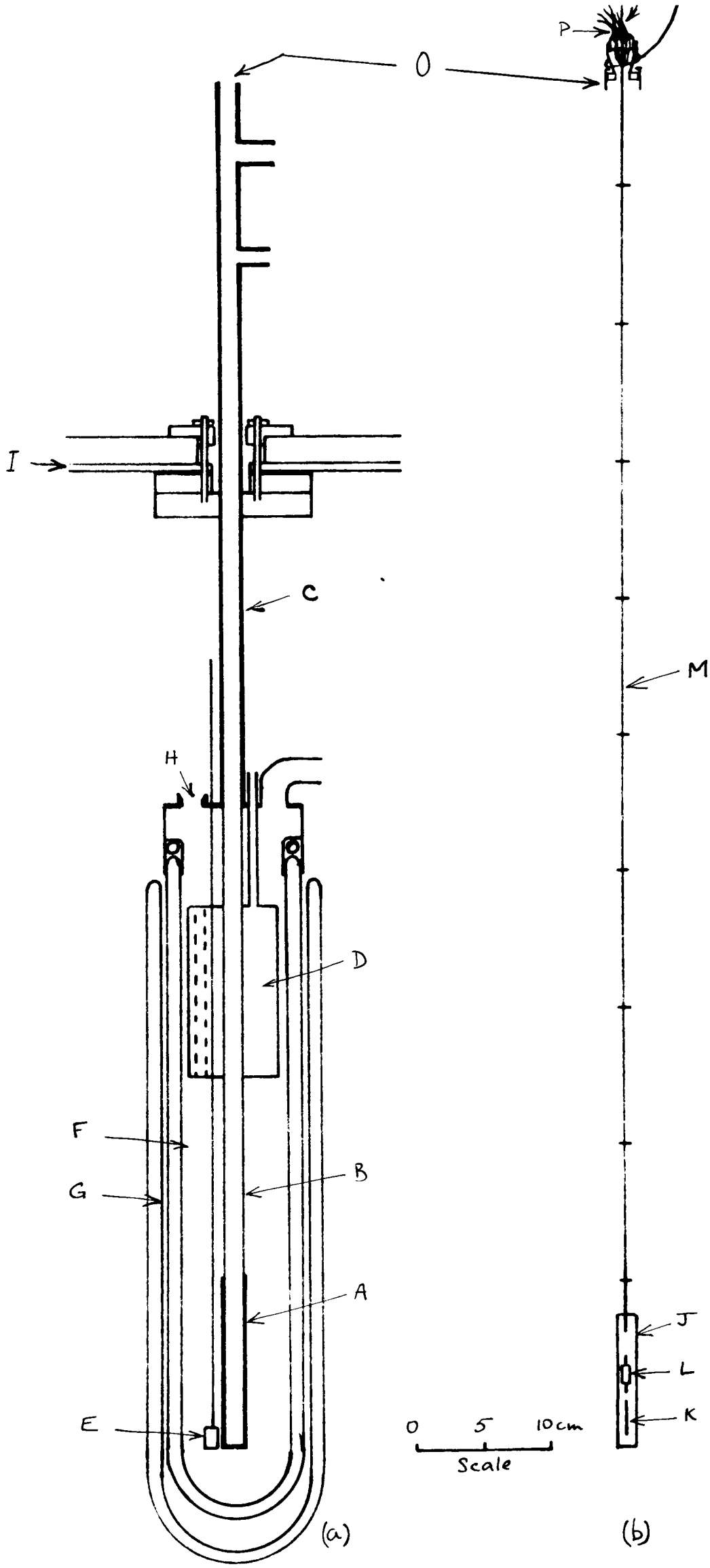
Further details regarding the construction and operation of glove-boxes can be found in the paper by Lord and Waldron (1957) or in papers read at the Glove-Box Symposium, 1958 (ed. Walton).

2.3.2. The Cryostat.

The principal factors influencing the design of the cryostat were as follows:

1) operation in the temperature range 1.4 to 4.2°K., yet flexible enough for use at all temperatures up to room temperature.

2) simplicity of operation as far as possible. For example



A copper } main
B g.silver } Cube
C brass
D liq.N_2 container
E gas thermometer
F inner (He) Dewar
G outer (N_2) Dewar
H Hole for siphon
I shell of glove-box
J specimen holder
K specimen
L carbon resistor
M 2mm g.s. tube
N nylon cord to pulley
O 'O'-ring seal
P black-wax seal
R leads

FIG. 2.4 Approximate Scale Drawing of the Cryostat

the handling of liquefied gases is best done outside the box.

3) straightforward introduction and removal of specimens.

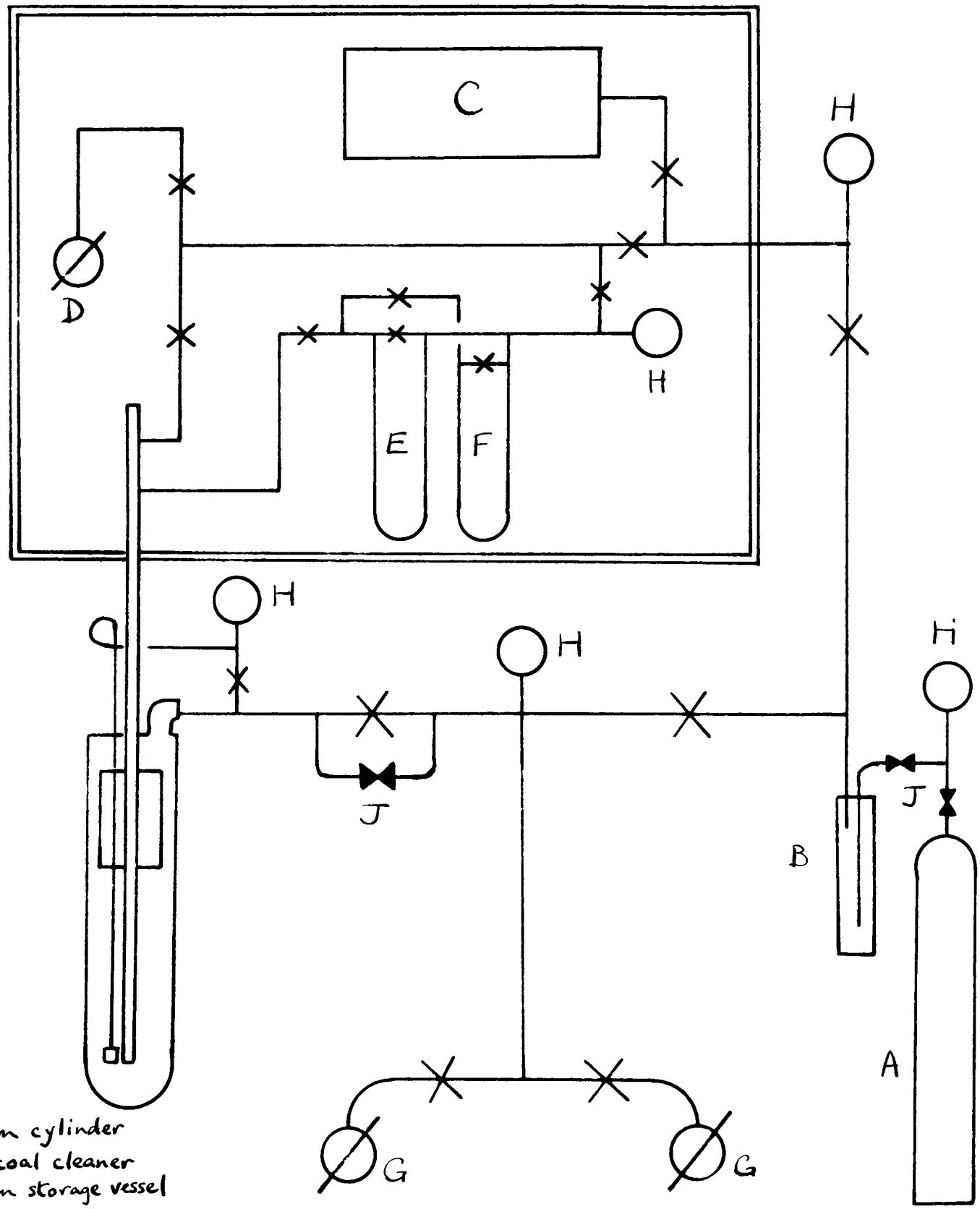
4) ease of repair or modification to the cryostat without having to take the glove-box to a frog-suit area.

5) preferably of such a shape that magnetic experiments could be carried out at a later date.

The design adopted largely met these requirements, and a description of it will now be given.

The main feature of the cryostat (fig. 2.4) was the long central tube, closed at its lower end, which passed vertically downwards through the floor of the glove-box. The inside of the tube, being a part of the glove-box, was "active"; but, since it was arranged that the cryogenic services were all outside this tube, modification or repair of the cryostat itself could therefore be carried out without disturbing the glove-box. The purpose of the tube was thus to cool specimens hanging inside it, by the employment of liquefied gases on the outside, and, in the case of experiments conducted below $4.2^{\circ}K$, to enable the specimen to be in intimate contact with liquid helium which had been condensed there.

The diameter of the tube was 15 mm. and it was almost



A helium cylinder
B charcoal cleaner
C helium storage vessel
D DRI rotary pump
E mercury manometer
F oil manometer
G N.G.N. rotary pumps
H vacuum & pressure gauges
J needle valves

FIG. 2.5 Simplified Flow Diagram

illustrating distribution of apparatus inside and outside of the glove-box

a metre in length. The upper half was made of brass but the lower half was of 15 mm. German silver tubing, with copper forming the bottom 13 cm. It was within this copper part that the specimens were suspended and the helium condensed. The top of the long tube led to a vacuum system, the helium gas supply and oil and mercury manometers (fig. 2.5). These manometers and the entire vacuum system, including a 60 litre per minute DR1 direct drive Metrovac rotary pump, were actually inside the glove-box. The DR1 was chosen for its relatively quiet running and because it had no belt drive. Before the box went active, an Edwards 1 8C 50 gave a lot of belt and motor trouble. Also within the box was an 18 litre helium storage vessel, which was filled via a charcoal cleaner to a pressure of nearly two atmospheres before a run from a high pressure helium cylinder outside. A woven-fibre-glass filter, incorporated in the line from the external helium supply where it entered the box, prevented any possibility of egress of activity from the box. O-rings were copiously used in this vacuum system so that it could readily be dismantled, if necessary, and posted out in sections.

Around the middle of the main central tube and inside the inner Dewar was a brass container that could be filled with liquid nitrogen. This served to reduce heat leaks

down the thin-walled 15 mm. German silver tube, and also acted as a radiation shield for the liquid in the Dewar.

All liquid helium had to be brought from the National Physical Laboratory and it normally arrived in 15 litre Dupree-Swift transport Dewars. From one of these Dewars liquid helium was siphoned into the inner monax Dewar of the cryostat using a detachable siphon. Here, it could be pumped by an external vacuum system, consisting of two 340 litre per minute rotary pumps running in parallel. The outer Dewar of the cryostat was for liquid nitrogen.

A small gas thermometer was also included in order to give a continuous indication of the temperature within the helium Dewar.

The specimen was mounted in a holder (section 2.7) along with a carbon resistor and several thermocouples. This holder was attached to the lower end of a long 1 mm. diameter German silver tube, which passed down the centre of the cryostat (fig. 2.4(b)). Thin metal discs, with small holes in them, were fixed to the tube at 10 cm. intervals to serve the dual purpose of guides for the leads and radiation shields for the liquid helium in the cryostat tube. At the time, there were in the apparatus eight insulated 40 S.W.G. constantan wires and three copper-constantan thermocouple pairs, which all passed into

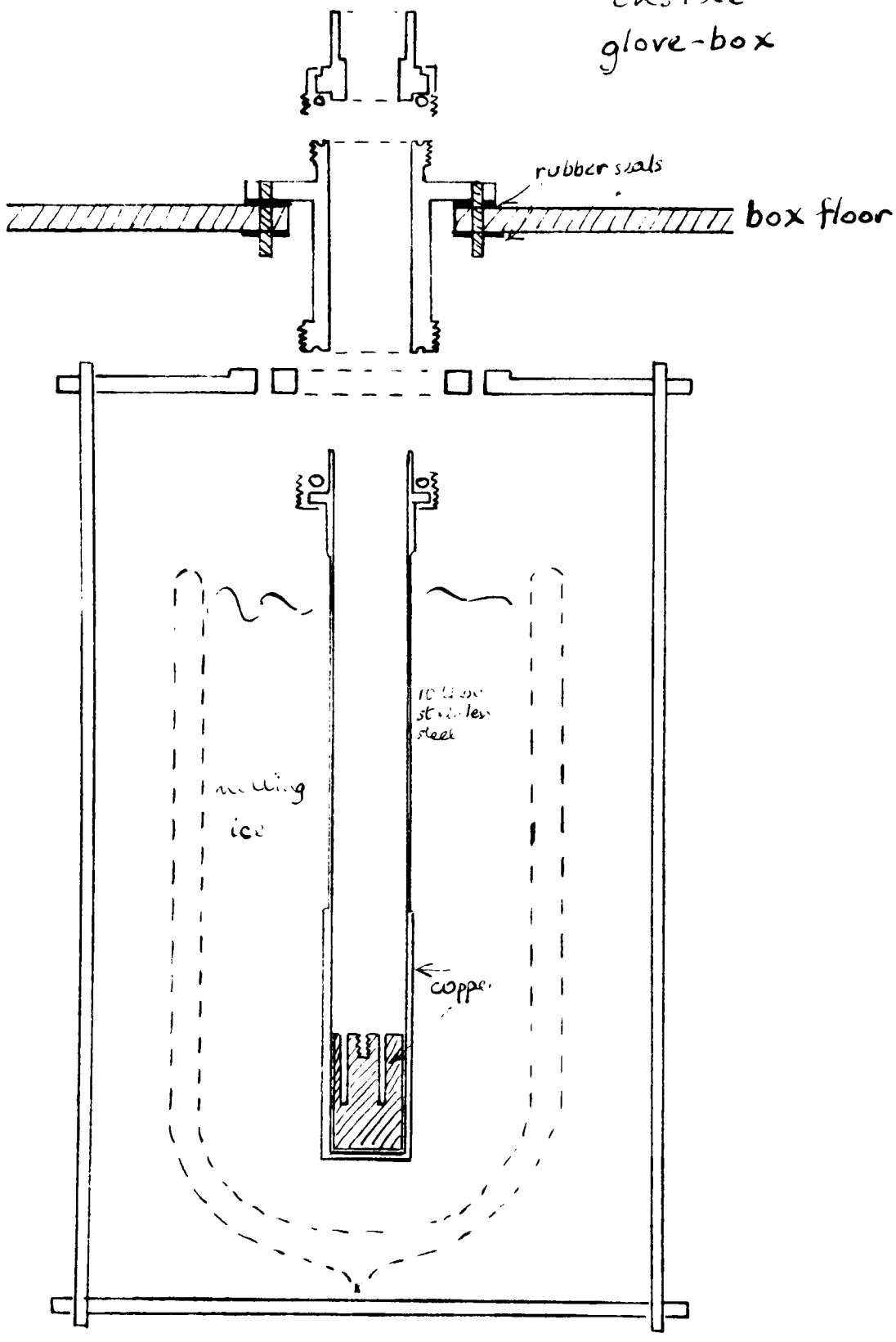


FIG. 2.6 Cold Junction of Thermocouples

the cryostat tube at its top through a black-wax seal. This whole assembly of specimen holder, German silver tubing and leads, including the black-wax seal, was lifted into the cryostat by the use of a pulley situated in a tower in the roof of the glove-box.

The cryostat was hung and mounted from the glove-box floor in such a way that should any major modification to the active part of the cryostat have become necessary, it would have been possible to have removed the entire cryostat by standard P.V.C. bag techniques and taken it to a laboratory fume cupboard.

Projecting downwards from the floor of the glove-box was a thin-walled stainless-steel and copper tube (fig.2.6). This formed the cold junction for the three copper-constantan thermocouple wires. The six junctions were situated in a copper block at the bottom of the tube, which was surrounded by a Dewar of melting ice. Thermal contact between the bath and the thermocouple junctions was clearly good since mercury-in-glass thermometers, placed in the ice and copper block, indicated the temperature of each to be the same. Furthermore, no thermal e.m.f. was obtained on putting the variable junctions of the thermo-couples into the lower end of the cryostat tube, around which also there was melting ice. This was important

since, when calibrating the thermocouples (section 2.5), it was assumed there existed no temperature gradient between them and the constant temperature bath.

The remaining leads from the cryostat were joined to 34 gauge copper wires at a tagboard, immersed in oil in a small Dewar situated in the glove-box. All the copper wires (14 in all) then passed from the box into the laboratory through a neoprene rubber seal set in the side of the glove-box.

2.4. General Procedure.

The cryostat was firstly precooled to 77°K, the specimen being in a helium atmosphere. Liquid helium was then siphoned into the inner Dewar from the transport Dewar. Pumping on this liquid helium was then commenced, and helium was condensed into the copper extension of the cryostat by passing in gas at a small overpressure. Usually, 20 to 25 cc. were liquefied in this way. The temperature of this internal liquid helium was then controlled by pumping on that in the helium Dewar. Since the Dewar could hold $1\frac{1}{2}$ litres, temperatures below 4.2°K could easily be maintained for six hours or more. Manual control of a 1 in. Saunders valve and a needle valve enabled any temperature to be maintained within limits of

±0.005°K for whatever length of time was desired, though 30 minutes was the longest that was ever attempted. As a rule, liquid helium was ordered in 10 litre quantities, this being sufficient for about three long runs spread over a week.

Once the liquid helium level had fallen below the bottom of the copper part of the cryostat, careful control of the pumping speed, coupled with the heat leak down the cryostat, allowed a controlled slow rise in the temperature of the specimen to be achieved. In fact, as long as some liquid helium remained, this rate of warming could be made as slow as was required. A rise from 4° to 20°K in two hours, for instance, was readily attained. With care, steady temperatures between 4° and about 12° could be held in rather unstable equilibrium for several minutes. When, finally, the last of the liquid helium had evaporated, the helium Dewar was evacuated and the specimen allowed to warm slowly to 77°K. Removal of the outer liquid nitrogen jacket, and emptying of the liquid nitrogen can, enabled the warming to continue to room temperature. Under these conditions, the warming from 4°K to room temperature took 7 to 10 hours. Faster rates could be obtained, when necessary, by electrical heating in the helium Dewar.

Another method of ensuring an initial slow temperature

rise from 4° was also employed from time to time. A lead cylinder, 18 cm. in length and 1800 gm. in weight, was suspended concentrically around the cryostat tube. Liquid hydrogen had now to be used as an intermediate cooling stage. About 1/2 litre of liquid hydrogen was evaporated in cooling the lead from $77^{\circ}K$ to $20^{\circ}K$ and then about 1/2 litre of liquid helium in bringing the temperature to $4^{\circ}K$. Then, after the final evaporation of helium, the large thermal capacity of the lead ensured that the rate of warming was slow and uniform. $20^{\circ}K$ was then reached in one hour and $77^{\circ}K$ in three hours.

On one occasion, when it was desired to reach a temperature of $360^{\circ}K$ ($87^{\circ}C$)., this was achieved by heating water in the inner Dewar with a small immersion heater.

This apparatus was used for determining the electrical resistivity of several radioactive metals and alloys, and its flexibility was further illustrated by the later measurement of thermoelectric powers also (section 2.9). It can, in addition, be used for the study of the Hall effect of radioactive substances since the cryostat, if a single narrow-tailed Dewar is used, can pass through a $4\frac{1}{2}$ cm. pole gap of an electromagnet.

The design also lends itself with little alteration to the measurement of magnetic susceptibilities by inhomogeneous field methods.

2.5. The Measurement of Temperature.

Use was made of three quite different temperature-dependent properties of different substances as thermometers over the temperature range from 1.4°K to room temperature. The problems associated with each will be discussed in turn.

2.5.1. Liquid Helium Temperature Range.

Below 4.2°K the specimen was always totally immersed in liquid helium, the temperature of which was obtained by measuring the vapour pressure and employing the "agreed" vapour pressure tables of van Dijk et al (1958). Because of the limited space available in the glove-box, the mercury and oil manometers were restricted to 30 cm. in length. A vacuum gauge was therefore employed for pressure measurement between 300 and 760 mm. Hg., i.e., between 3.35 and 4.21°K. Pressures in this region could only be read to the nearest cm., viz. to the nearest 0.02°K., but this was quite accurate enough for our purposes. The oil manometer contained butyl phthalate, and was calibrated periodically by comparison with the mercury manometer.

The temperature of the liquid helium bath was maintained constant for each reading by the regulation of the pressure over the bath by controlling the pumping

speed. Above the lambda point, the required temperature was always approached from above to avoid the possibility of supercooling the liquid beneath the surface.

Since Pu continuously releases energy at the rate of about 2 milliwatts per gm., the question arises whether a Pu specimen can be taken as being at the temperature of the liquid helium or not. A calculation of the Kapitza boundary heat resistance between 2 gm. of Pu* and liquid He II, however, gives a temperature difference which is less than $0.01^{\circ}K$, even at the lowest temperature attainable (i.e., at $1.4^{\circ}K$).

2.5.2. $4.2^{\circ}K$ to $20^{\circ}K$.

This temperature range was covered by the use of carbon composition radio resistors.

A 1/4-watt 56 ohm nominal resistance LAB resistor** was tried first of all, as having a suitably large temperature coefficient over the required temperature range.

To calibrate the thermometer, the familiar three-constant equation of Clement and Quinnell (1952) was tried

$$\log R + \frac{k}{\log R} = A + \frac{B}{T} \qquad \ldots(9)$$

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* Most specimens weighed 2 gm. or less

** Manufactured by the Radio Resistor Co Ltd., Abbey Gardens, London N.W.8.

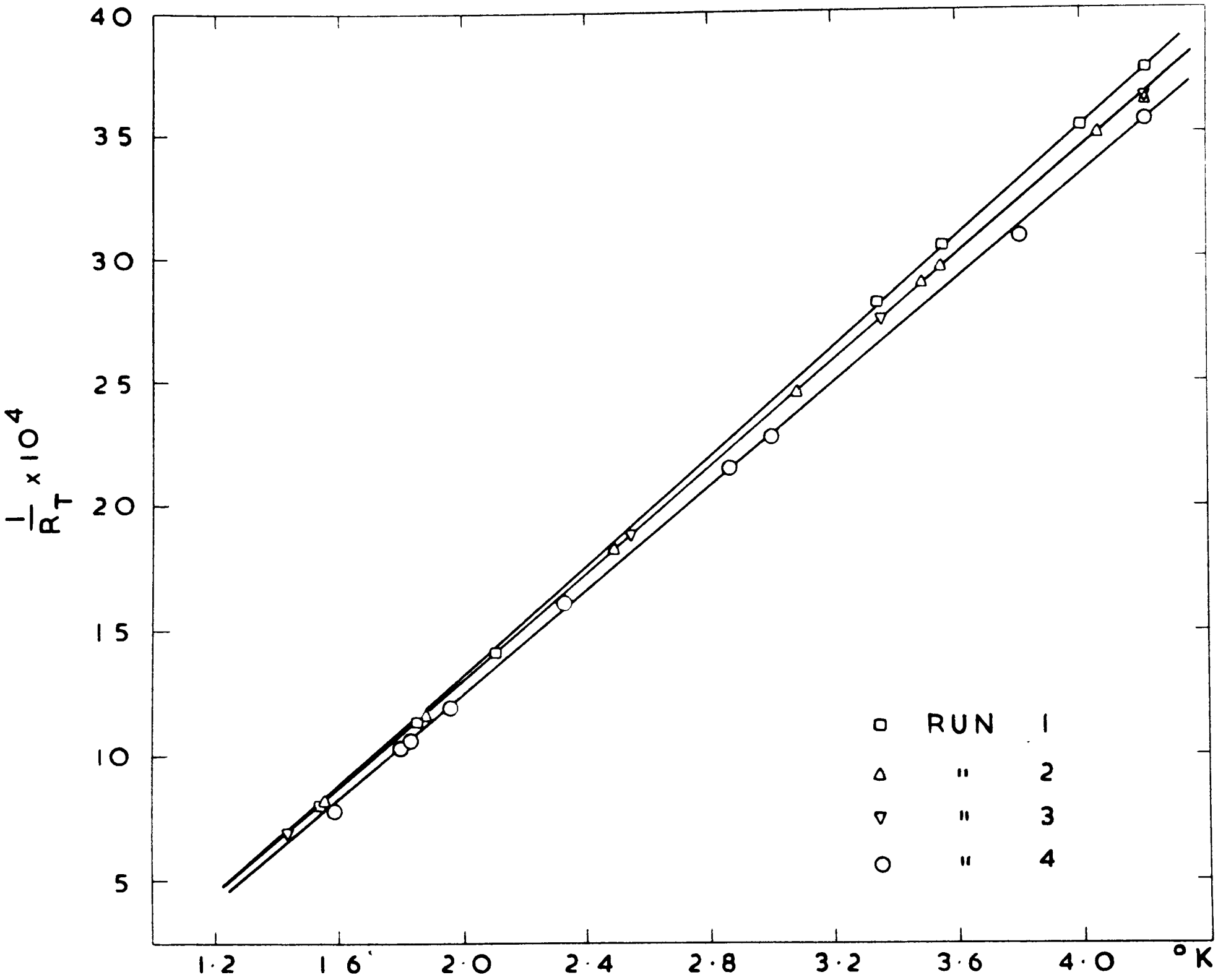


FIG. 2·7. RESISTANCE OF 56 ohm $\frac{1}{4}$ WATT. LAB. RESISTOR

and also several related two- or three-constant formulae, by calibration at three points such as 2.1, 4.2, 20°K or 1.6, 2.1, 4.2°K. Comparison was then made with temperatures obtained from the helium or hydrogen vapour pressure scales. Good fits could not be obtained, and this resistor had to be rejected for use as an interpolation secondary thermometer for the 4° to 20°K temperature range; but it was found to possess a most useful property which it is worth recording. This property does not appear to have been observed before*.

Between the temperature limits obtainable with liquid helium in the cryostat, viz. 1.4 and 4.2°K., it was found that the temperature was closely inversely proportional to the resistance i.e., the temperature was given by

$$\frac{A}{R} = T + \theta \qquad \ldots(10)$$

where A and θ are constants, and $\theta \sim -0.8$.

The results of four runs are shown in fig. 2.7, and it is seen that all the straight lines intersect on the temperature axis at ~ 0.8°K. If, now, reduced resistance values are employed, obtained by dividing $R_{4.2}$ into R_T for each curve in turn, we find that the four straight lines

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* Lounasmaa (1958) found that a 1/4-watt LAB resistor displayed a constant $\frac{d}{dT}\left(\frac{1}{R-R_o}\right)$ between 5° and 12°K.

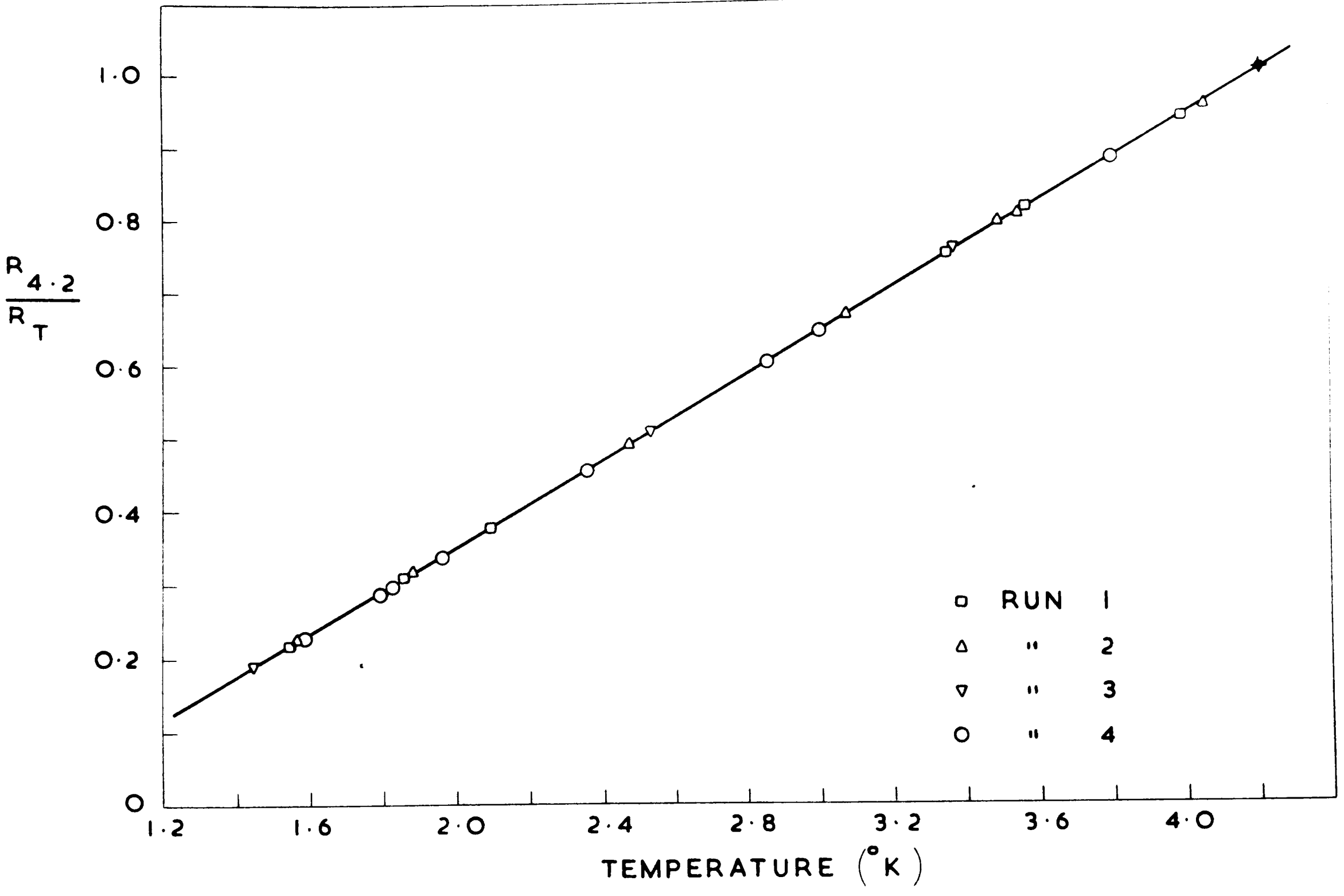


FIG. 2·8. REDUCED RESISTANCE vs. TEMPERATURE

(representing four entirely separate runs) coincide completely (fig. 2.8). Indeed, this final straight line graph was found to hold for that particular resistor on all subsequent runs, only one calibration point being required for any one run (this was always conveniently taken as 4.2°K). This resistor naturally proved extremely useful as a secondary thermometer at helium temperatures, and, because of it, several other similar resistors were also checked. The relationship given by equation (10) was in fact also found to hold for an identical resistor taken from the same batch, but unfortunately carbon resistors taken from a fresh batch some months later did not follow equation (10) sufficiently well for use.

To cover the temperature range 4 to 20°K a 47 ohm, 1/4 watt Allen-Bradley carbon resistor was obtained. The use of these resistors is now well established, and good agreement with Clement and Quinnell's equation (9) was immediately found. It was calibrated at ~ 2.1, 4.2 and 20°K on every run to obtain the constants A, B and k and also at several points between 2 and 4°K, and agreement with the formula checked. The formula was then used as an interpolation formula between 2 and 20°K. Now, according to Clement and Quinnell, temperatures calculated by their equation are correct to within ±0.5%, and

reproducible to within ±0.1% from run to run. So, since we were making dynamic measurements of the electrical resistance of our specimens, we felt justified in assuming that any error in temperature measurement introduced by interpolating in this way, would be less than that associated with the imprecision arising from the time delay between obtaining a specimen resistance measurement and the corresponding temperature measurement (see section 2.7.2. for further details on this). The maximum error involved was unlikely to be greater than ±1/4°K with the slow rates of warming actually achieved.

2.5.3. 20°K to Room Temperature.

Copper-constantan thermocouples were employed for the measurement of temperature over this range. Since replacement of wires in the glove-box would be extremely laborious and tedious, it was desirable that the thermocouples should have a long working life by remaining reproducible in calibration. It was also envisaged that they might play a major part in a method for determining the thermoelectric powers of the actinide specimens (section 2.9). They were therefore selected with great care from the point of view of uniformity in composition in the following manner.

A polythene tube was bent into a U-shape and placed

in a Dewar of liquid nitrogen. A loop of the thermocouple wire, several feet long with a galvanometer in the circuit, was then passed very slowly through this tube and the indications of the galvanometer observed. Kinks or local inhomogeneities in composition of the wire displayed themselves by excessively deflecting the galvanometer, and such wire was then rejected.

The variable-temperature junctions of the copper-constantan thermocouples were made by spot-welding in the argon atmosphere of the glove-box. The welder used was the one devised by Hill (1959), in which the spark is produced by the discharge of a bank of condensers. This spot-welder is very suitable for welding together fine wires in an easily controlled and reproducible manner. Thermocouple bead diameters were generally able to be made as small as 1/5 mm. This was important, because the e.m.f. of a thermocouple measures the temperature of the junction at the point where the two wires separate, so that with a large bead there could be an appreciable temperature gradient across it. Also, in the case of Pu with its high self-heating, there is necessarily a small heat leak away from the sample down the thermocouple wires. On this account the wires used (40 S.W.G.) were of the smallest cross-section that could conveniently be

manipulated in a glove-box; they were, furthermore, thermally insulated right up to the junction beads themselves.

Three copper-constantan thermocouples of 40 S.W.G. wire were prepared in this way. The thermocouple leads were, in fact, continuous all the way to the cold junctions which, as explained in section 2.3.2, were situated in a tubular extension beneath the glove-box floor. The leads then passed to a Cambridge microvolt vernier potentiometer.

The calibration of the thermocouples was done before every run by constructing a deviation curve against the data of Giauque, Buffington and Schulze (1927). Initially, the calibration points were the sublimation point of carbon dioxide and the boiling points of oxygen, nitrogen and hydrogen; the deviation plots were found to be almost exactly straight lines. In practice, the CO_2 point was determined only at infrequent intervals, due to the constancy with which the calibrations were maintained, so that as a rule calibrations were performed at only 77 and 20°K with respect to the ice-point. Over a period of two years the calibration of the thermocouples proved extremely consistent and reliable. The liquid hydrogen calibration for instance, remained within ±1 microvolt of 6317 microvolts with respect to 0°C throughout, even though the junctions were remade on several occasions. This was probably due to

the careful choice of wires and the ability to make almost strain-free junctions.

The CO_2 point, by the way, is not an easy one to obtain accurately, for it is found that in a Dewar of crushed solid CO_2 the apparent temperature of sublimation increases steadily with time, and that more than 24 hours are needed for equilibrium to be reached. This is caused by air, trapped in the powder, taking a long time to diffuse out. However, with an 18 watt heater at the bottom of the CO_2 bath a steady stream of CO_2 vapour is given off, and equilibrium conditions are reached in about 15 minutes (cf. Scott, 1941).

Other workers besides Giauque et al (1927, a,b) have given copper-constantan thermoelectric force tables that extend to 15°K or lower. These are Aston, Willinghanz and Messerly (1935), Southard and Milner (1933) and Powell, Bunch and Corruccini (1961). Adams' (1926) tables only extend to ~50°K, and Southard and Andrews' (1929) to 85°K. However, we took the tables of Giauque, Buffington and Schulze (1927), as corrected by Giauque, Johnston and Kelly (1927), as standards for constructing our deviation curves because

(a) these deviation curves were found to be almost straight lines;

(b) the calibration of our thermocouples corresponded more closely to these than to any other set of tables (except Powell et al's) - this was evidently due to similarity in the composition of the constantan wires.

(c) Ahlberg and Lundberg (1935) found that the empirical relation $E = A + BT^2 + CT^3 + DT^4$ fitted Giauque's curves to well within the limits of accuracy of Giauque's experimental measurements (the maximum deviation of $0.05^{\circ}K$ came between 24 and $35^{\circ}K$).

The thermoelectric power of constantan, being very large and increasing rapidly with temperature, dominates at all temperatures that of pure copper, which is small and varies little with temperature. Some apparently high purity samples of copper, however, have been found to possess anomalously large thermoelectric powers centred around $9^{\circ}K$ (Gold, MacDonald, Pearson and Templeton, 1960); and this has been related to the presence of trace amounts of iron. While there was evidence that our copper wire had such an anomaly, it was not such as to noticeably impair its use as thermocouple wire at $20^{\circ}K$ or above. We issue the warning, though, that, if copper is to be employed as a thermocouple element below $\sim 20^{\circ}K$, it must be particularly carefully selected.

2.6. Specimen Preparation.

The source, dimensions, density, treatment and (where known) spectrographic and chemical analyses of the specimens will be given in the next chapter when presenting the results.

Most specimens were in the form of rods from 15 to 50 mm. in length, and from 1 to 2.5 mm. in diameter. The actinide elements generally have high resistivities, even at low temperatures, so that resistance measurement on these rather short, thick samples was no great problem. For convenience, some of the specimens, originally prepared and used for resistance experiments, were also employed for the thermoelectric power experiments. Since the actinides also have relatively poor thermal conductivities, a suitable temperature gradient for thermoelectric power work could still be set up without difficulty along even the shortest specimens. The extreme case was Np 3 , where due to the limited amount of metal available, the specimen length was only 15 mm. and the distance between the thermocouple probes just 9 mm.

The samples were prepared by gravity casting under vacuum into precision-bore silica tubes, by extruding or simply machining. The arc-melting of the original billets

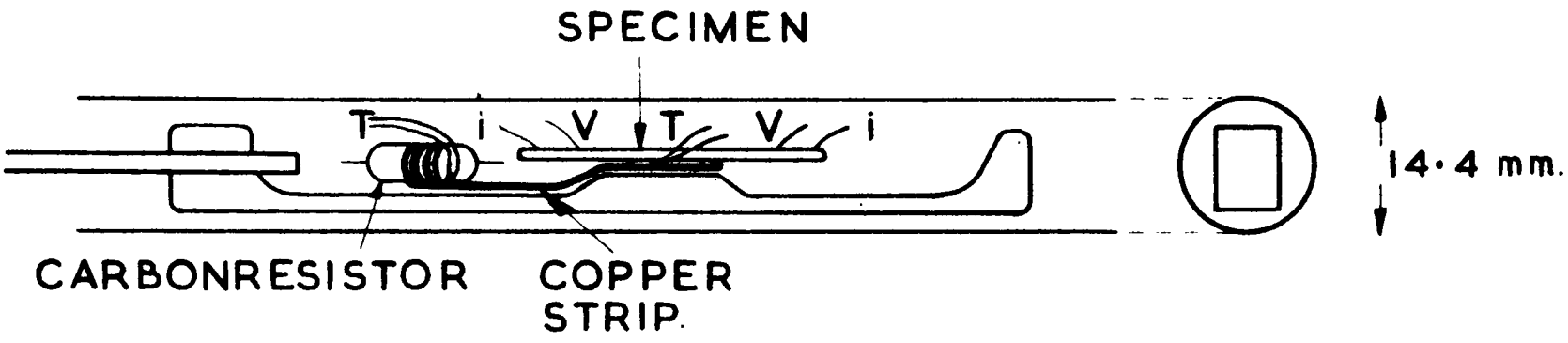


FIG. 2·9. (a) SPECIMEN MOUNTING.

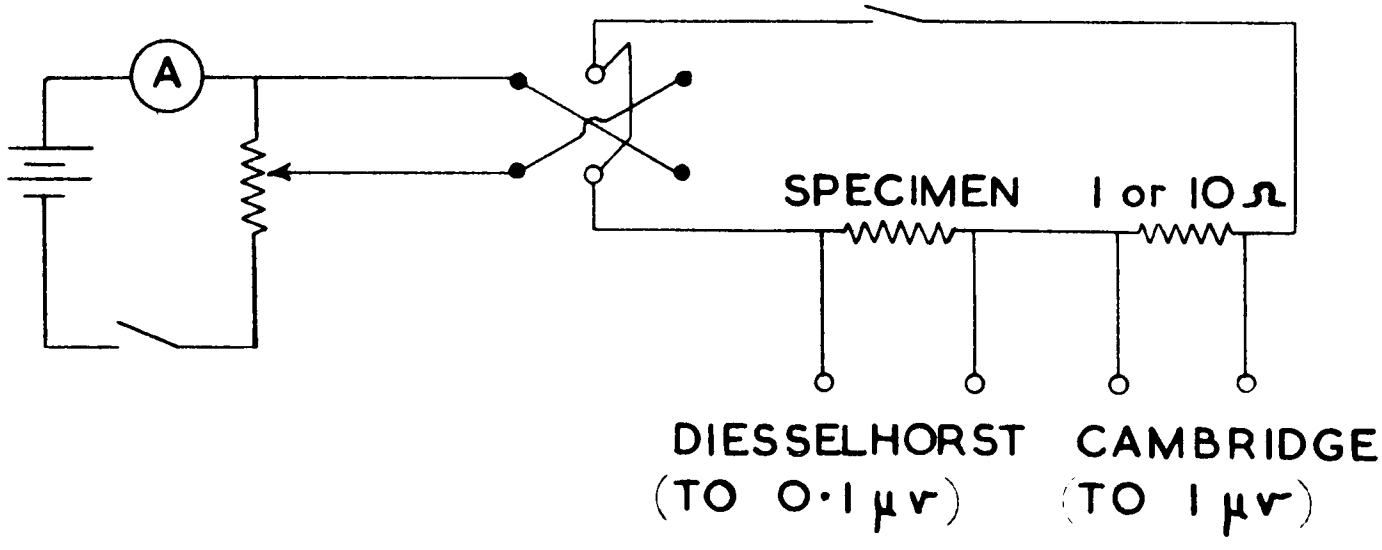


FIG. 2·9. (b) BASIC CIRCUITRY

was done in an argon arc furnace, with zirconium as a getter. Densities were determined by the well-tried displacement method, the liquid employed being ethylene dibromide ($\rho \sim 2.2$ gm. per cc.). As a rule, accuracy was to within 0.1%, but in a few cases, where the sample weight was less than the weight of the supporting stirrup, it was only about 0.5%. Both the arc-furnace and the Sartorius balance were set up in glove-boxes, forming part of the laboratory's series of Pu - alloy - preparation glove-boxes.

2.7. Specimen Mounting for the Electrical Resistivity Experiments.

Specimens were mounted in a perspex holder, which was attached to the lower end of the long central 2 mm. German silver tube (fig. 2.9(a) and fig. 2.4(b)).

The variable junction of one thermocouple was always placed in contact with the middle of the specimen, while a second thermocouple was usually positioned near or at one end, or else perhaps on the carbon resistor. The insulated copper wire, which was bound to the body of the carbon resistor, was soldered to a strip of 1/2 mm. thick copper, which under-ran the central part of the specimen. Thermocouples on the resistor and on the specimen rarely indicated a temperature difference of as much as 1/4 to 1/2

^{o}K at 20^{o}K, even under high warming-up rates. The specimen temperature was therefore taken as that indicated by the carbon resistor, since most warming rates were, in fact, quite slow and the accuracy of temperature measurement by the resistor was anyway only to the nearest 1/4^{o}K (section 2.5.2).

Before mounting a specimen, the mean diameter was always determined using a micrometer. The accuracy with which this could be done varied from one specimen to another, since not all specimens were perfectly regular rods. The other dimension required for the form factor, viz., the distance between the potential leads, was determined using a travelling microscope, which had to be mounted outside the glove-box window. The main uncertainty involved in making this measurement arose in deciding exactly where each potential lead was attached to the specimen. Even so, it is unlikely that any resulting error in the form factor from these room temperature measurements was greater than 1/4%.

The constantan current and potential leads were attached to the specimen by spot-welding (section 2.5.3). This had the advantage over the use of spring-loaded contacts of reducing contact resistance, though the time spent in mounting a specimen was considerably greater.

Since the leads are rigidly fixed to the specimen, the form factor is a function of temperature, due to the thermal expansion of the specimen. We have not, however, applied a correction because of a lack of reliable data on the thermal expansion coefficients. There is evidence that the expansion coefficient in U (Schuch and Laquer, 1952) changes sign at low temperatures (and also perhaps in Pu (Sandenaw, 1960)), but these effects are very small compared with the high temperature coefficient of resistance. The maximum error in the magnitude of the absolute value of the resistivity at helium temperatures, arising from the neglect of this correction, would probably be 1%.

2.8. The Measurement of the Electrical Resistance.

Electrical resistance measurements that have to be made over wide ranges of temperature are most conveniently made dynamically. Whereas rapid measurement is obviously an essential requirement, a sufficiently high degree of accuracy and sensitivity must at the same time be maintained. A potentiometer provides the best means of achieving this, with the sample arranged as a four-terminal resistor.

A Diesselhorst thermoelectric free vernier potentiometer was used for the measurement of potential differences

down to 0.1 microvolt. The sensitivity of the Tinsley LS 4789 galvanometer employed with it was 10 mm. per microvolt, with the usual one metre beam throw (period 4 secs). The potential differences to be measured at helium temperatures were always at least 10 microvolts in magnitude and often very much more. Assuming then that a 1/2 mm. deflection of the beam was readily observable, this represented an accuracy of 1/2% or better in measurement at these temperatures.

The potential difference across the specimen was compared with that across either a 1 ohm or a 10 ohm standard resistance, the latter potential difference being read on a Cambridge vernier potentiometer to the nearest microvolt (thus giving the current to 5 significant figures). Fairly uniform specimen currents of between 10 and 50 milliamps were obtained by grouping 6 to 12 two-volt accumulators in pairs or in threes and arranging them in parallel.

An important problem in the dynamic measurement of resistance is the reduction, or, if possible, the elimination, of the effects of unwanted thermal e.m.f's. For instance, the effect of the slight thermal gradient, invariably present along the length of a specimen that is slowly

changing in temperature, was eliminated by the use of a reversing switch included in the specimen current circuit (fig. 2.9(b)). Furthermore, in order to reduce possible spurious thermal e.m.f's in the switching gear as much as possible, this switch was a commercial Tinsley thermo-electric free one. It enabled the direction of the currents through the specimen and through the potentiometer to be changed rapidly and almost simultaneously. The sequence in which the measurements were taken in quick succession was as follows: p.d. across the standard resistance, p.d. across specimen, specimen thermocouple reading, reversed p.d. across specimen and lastly reversed p.d. across standard resistance.

2.9. The Thermoelectric Power Experiments.

The design of the cryostat had been such that thermoelectric power experiments could be set up with the addition of only quite a simple assembly within the cryostat tube.

The methods available fell into two classes:

(1) integral methods where the total e.m.f. between two junctions, one of which is held at a constant temperature, is measured;

(2) differential methods in which the temperature difference

between the junctions is kept small, and the power is taken as the measured e.m.f. divided by the mean temperature of the junctions.

In practice, method (1) would have involved either

(a) the setting up of a very long sample (~ 50 cm.) alongside Pb wire as a reference standard, with the variable junction at the bottom of the cryostat tube and the fixed junction maintained at room temperature,

or, preferably,

(b) a rather shorter sample with the fixed junction at the bottom of the tube (using liquid helium, hydrogen and argon successively as constant temperature baths) and with the variable junction some 20 cm. above it.

Compared with method 2 above, methods 1(a) and (b) prove rather more cumbersome in a glove-box, and method 2 was therefore adopted. Besides, it was known that only 2 or 3 cm. of Np, at most, would be available, so that a class 2 method would have to be employed for Np in any case. Furthermore, integral methods have the disadvantage that S is not given directly; but the experimentally determined E-T relationship has to be differentiated in order to obtain S, with a resulting loss in accuracy.

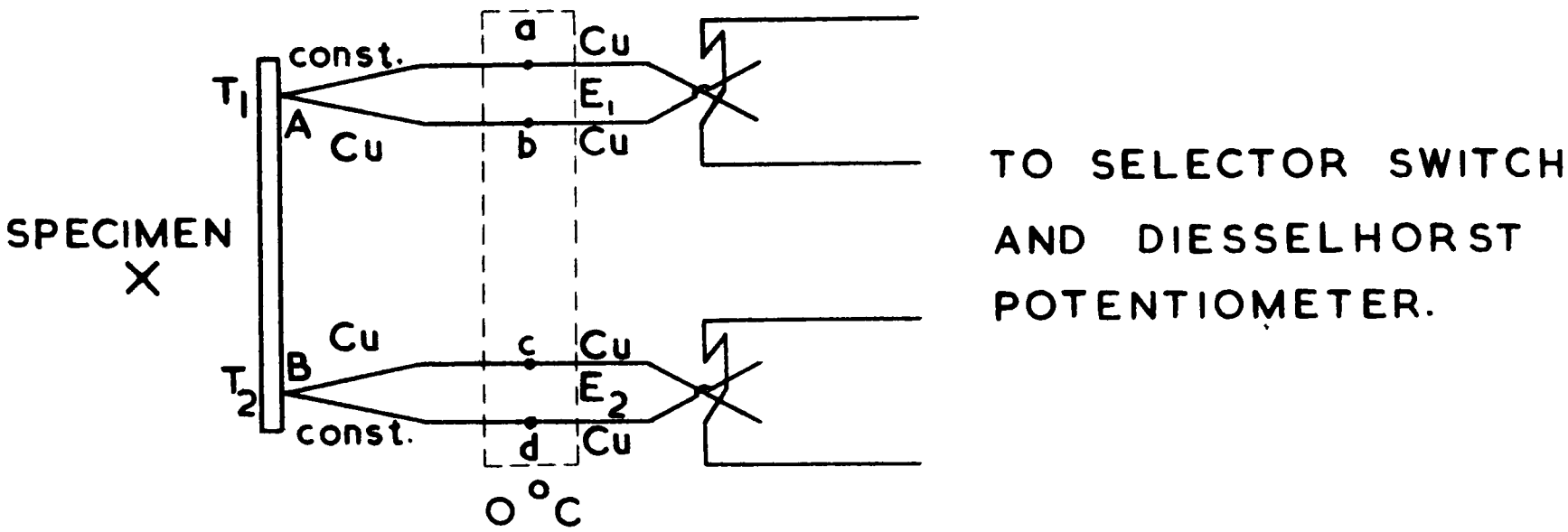


FIG. 2·10. (a) THERMOELECTRIC POWER-BASIC CIRCUITRY.

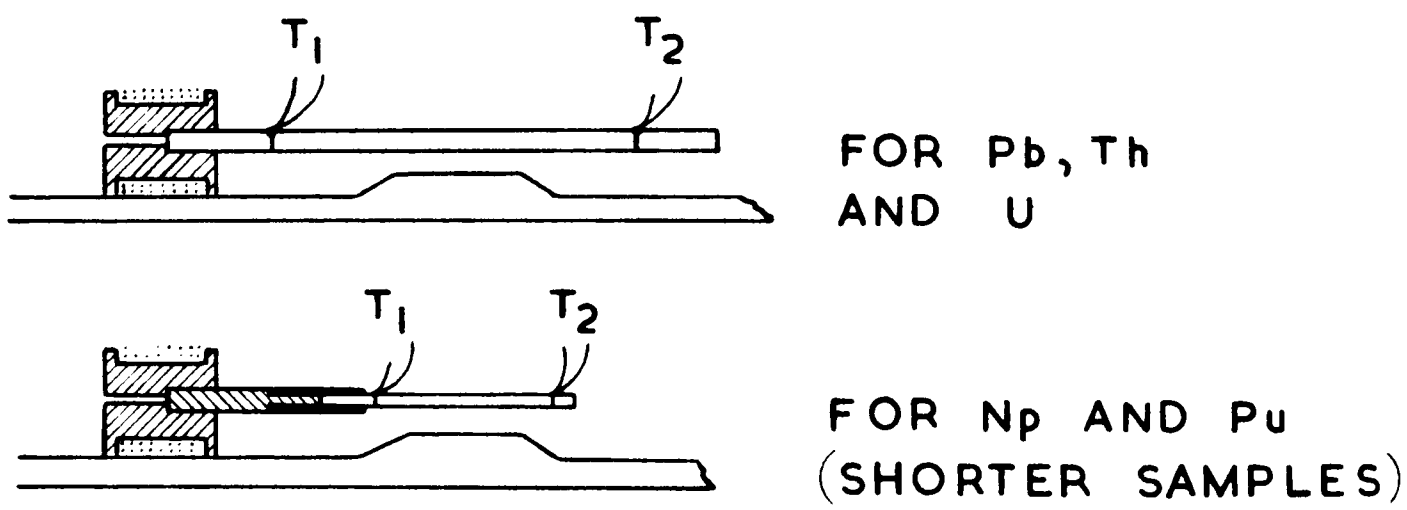


FIG. 2·10. (b) SAMPLE MOUNTING.

2.9.1. Description of Method.

The method of approach was similar in principle to that described by Middleton and Scanlon (1953).

The sample was in the form of a short rod X, along which a temperature gradient was set up. The temperatures T_1, T_2 at two points A and B of the rod were then measured by means of copper-constantan thermocouples situated at these points. These thermocouple wires, as explained in section 2.5.3, were continuous as far as their cold junctions. There, they joined on to copper wires leading directly to the switching system (fig. 2.10(a)). The p.ds between a and b, c and d, b and c &(though not strictly needed) a and d were measured in turn. We denote these by E_{ab}, E_{cd}, etc. respectively. Then, since E_{bc} and E_{ad} represent the thermal e.m.f. of the specimen against copper and constantan respectively for the small temperature difference $\Delta T = T_1 - T_2$, the corresponding thermoelectric powers are

$$S_{X-Cu} = \frac{E_{bc}}{\Delta T} \quad \text{and} \quad S_{X-const} = \frac{E_{ad}}{\Delta T}.$$

The thermoelectric power s_T of the copper-constantan thermocouples, corresponding to the mean temperature $T = \frac{T_1+T_2}{2}$, was next obtained from the calibration graph of

the thermocouples. The temperature difference ΔT was then given by

$$\Delta T = \frac{E_{ab} - E_{cd}}{s_T}$$

We therefore have for the thermoelectric power of the specimen relative to the copper of which the thermocouple was made

$$s_{X-Cu} = \frac{E_{bc}}{E_{ab}-E_{cd}} \cdot s_T \qquad \ldots(11)$$

To obtain the absolute power of the specimen, we must first know the absolute power of the copper. This was done by employing as a specimen spectroscopically-pure lead (section 4.1), the absolute power of which was known from the work of Christian et al (1958) and Borelius et al (1932).

2.9.2. Specimen Mounting.

The manner in which the samples were mounted is illustrated diagrammatically in fig. 2.10(b).

The temperature gradient along the specimen was produced by a small heater of 46 S.W.G. constantan wire (total resistance 800 ohms) wound on a copper former. The latter had a $2\frac{1}{2}$ mm. diameter hole drilled partially through it, into which one end of the Pb, Th or U specimens could be firmly placed. The Pu and Np specimens, however,

which were 37 and 15 mm. long respectively, were too short for this. A short length of copper rod was therefore used to carry heat from the heater to these specimens (fig. 2.10(b)).

In this method of measuring thermoelectric powers, it is essential that both thermal and electrical contacts between the sample and the thermocouple junctions be very good. Spot-welding the thermocouple beads to the specimen proved unsuccessful, one or the other of the thermocouple wires generally melting through. After some experimenting, the following practice was adopted. A shallow groove was filed round a circumference of the specimen, and into it was welded a complete loop of 36 S.W.G. copper wire, spot welds being done at about half a dozen points. The thermocouple bead was then soldered to the copper loop with soft-solder or Wood's metal, so that the tiny bead was flush with the surface of the specimen.* These precautions, viz. the employment of small beads sunk flush to the surface of the specimen and the use of fine thermocouple wires, ensured that the actual surface temperature would be measured as closely as possible. In addition, all experiments were carried out with the specimens in vacuo,

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* In the case of the lead specimen, the thermocouple beads were soldered directly to the surface of the specimen with Wood's metal.

in order to remove undesirable effects that might otherwise have been caused by convection currents.

2.9.3. The Measurement of the Thermoelectric Power.

The switching system was so arranged that the e.m.f. of either thermocouple, or the e.m.f. of the sample with respect to either thermocouple wire, could be measured in turn on the Diesselhorst thermoelectric free potentiometer. Since the deflection of the galvanometer, corresponding to a p.d. of 0.1 microvolt in the specimen-copper circuit, was 4 mm., a change in reading equivalent to 0.01 microvolt could just about be estimated.

The Tinsley thermoelectric free reversing switch was able to reverse the current from all four wires a, b, c and d, and the current in the potentiometer simultaneously. The effect of stray thermal e.m.f's in the selector switch and external connections to the potentiometer were therefore much reduced. However, any parasitic thermal e.m.f's present along the lengths of the thermocouple wires would be unidirectional. It was possible to allow for them, to some extent, by observing the thermal e.m.f. in the specimen-thermocouple wire circuit under conditions of zero temperature gradient along the specimen. In fact, it was often found that, at any given constant temperature,

the thermoelectric power was slightly dependent on the temperature gradient. This was due to a parasitic e.m.f. of about 0.1 to 0.25 microvolts superimposed on the much greater e.m.f. being measured. It was determined by plotting a graph of E_{bc} against various ΔTs, obtained in the region $\Delta T = 0$ to $5^{\circ}K$, and measuring the intercept on the E_{bc} axis. The corrected values of S so obtained were then found to be almost independent of ΔT. This showed, in addition, that there was little error in the measurement of ΔT. If, for instance, the observed ΔT had been underestimated at large ΔTs because of heat losses, this would have led to an increase in S with increasing ΔT.

This procedure was followed in all cases where static observations (by the use of constant temperature baths) were being made, but could not be undertaken in the case of dynamic experiments. The correction involved was usually very small, except in a few cases where E itself was nearly zero. As can be seen from the experimental results in Chapter 4, the points obtained dynamically lie on the same curves as those obtained statically, indicating that any errors from this effect are negligible.

During most runs the e.m.f. of the specimen-constantan thermocouple was not in fact measured. Measurements were

taken in the earlier experiments, but they appeared to be subject to more scatter than those from the specimen-copper circuit. Some determinations of the thermoelectric power of the specimen from $S_{X-const}$ were made from time to time, but only as a check on those obtained from S_{X-Cu}.

The sequence in which the measurements were generally taken was as follows (see fig. 2.10(a)): E_{ab}, E_{cd}, E_{ab} again, E_{bc} and E_{bc} with switch reversed. The readings were taken in quick succession, and it is not thought that the time delays involved introduced any serious errors. This is reflected in the generally good agreement between static and dynamic readings. The rate of warming employed in the warming runs was 30 to 40°K an hour.

Finally, we point out that, in this method of determinin thermoelectric powers, copper-constantan thermocouples can only be used below 30 to 40°K with rapidly lessening accuracy. The thermoelectric power of the thermocouples is only ~8 microvolts/°K at 30°K, compared with 20 at 100°K and 32 at 200°K. The e.m.f. associated with a given ΔT therefore becomes substantially smaller at the lower temperatures, so that, while most values of S_{X-Cu} are probably correct to within ±1/2 microvolt/°K, the accuracy would only be about ±1 below 40°K.

2.10. Experimental Accuracy.

The main sources of error in both the electrical resistivity and thermoelectric power measurements have already been indicated in the preceding pages. We will merely give a short summary here. The accuracies assigned to the various results will be given as the latter are presented in the next two chapters.

Random errors associated with the derivation of the electrical resistance were in general quite negligible. Except for some of the lower resistance specimens at the lowest temperatures, the currents employed were such that the potential drops across the specimen could be measured with 1/10% accuracy or better. The derived absolute resistivities at room temperature, however, in those cases where there was uncertainty in the form factor, were subject to greater errors than this. But, even in the most irregular rods, this was unlikely to have been worse than 1/4%. The fact that no allowance was made for the temperature dependence of the form factor involved a maximum error at helium temperatures of about 1% (section 2.7).

Temperatures derived from thermocouple or carbon resistance readings could be said to be accurate to the

nearest 1/2°K. Since readings were invariably taken dynamically, the uncertainty should perhaps be broadened to the nearest 1°K. Possible systematic errors are not considered to have been important.

In the thermoelectric experiments, both random and systematic errors would arise from stray e.m.f's superimposed on the one being measured. It is felt that the final data on the thermoelectric powers of the various specimens are correct to within ±1/2 microvolt/°K, though below 40°K it may be worse, viz. ~±1 microvolt/°K.

CHAPTER 3.

The Electrical Resistivity of the Actinide Metals from 0.75°K to 300°K

The experimental data obtained on the metals Th, U, Np and Pu will be presented in this chapter, together with some discussion of the results*. Further discussion will be held in Chapter 5.

The order in which we shall consider these metals, that of increasing atomic number, coincides with widening departure from normality so far as the electrical resistivity is concerned.

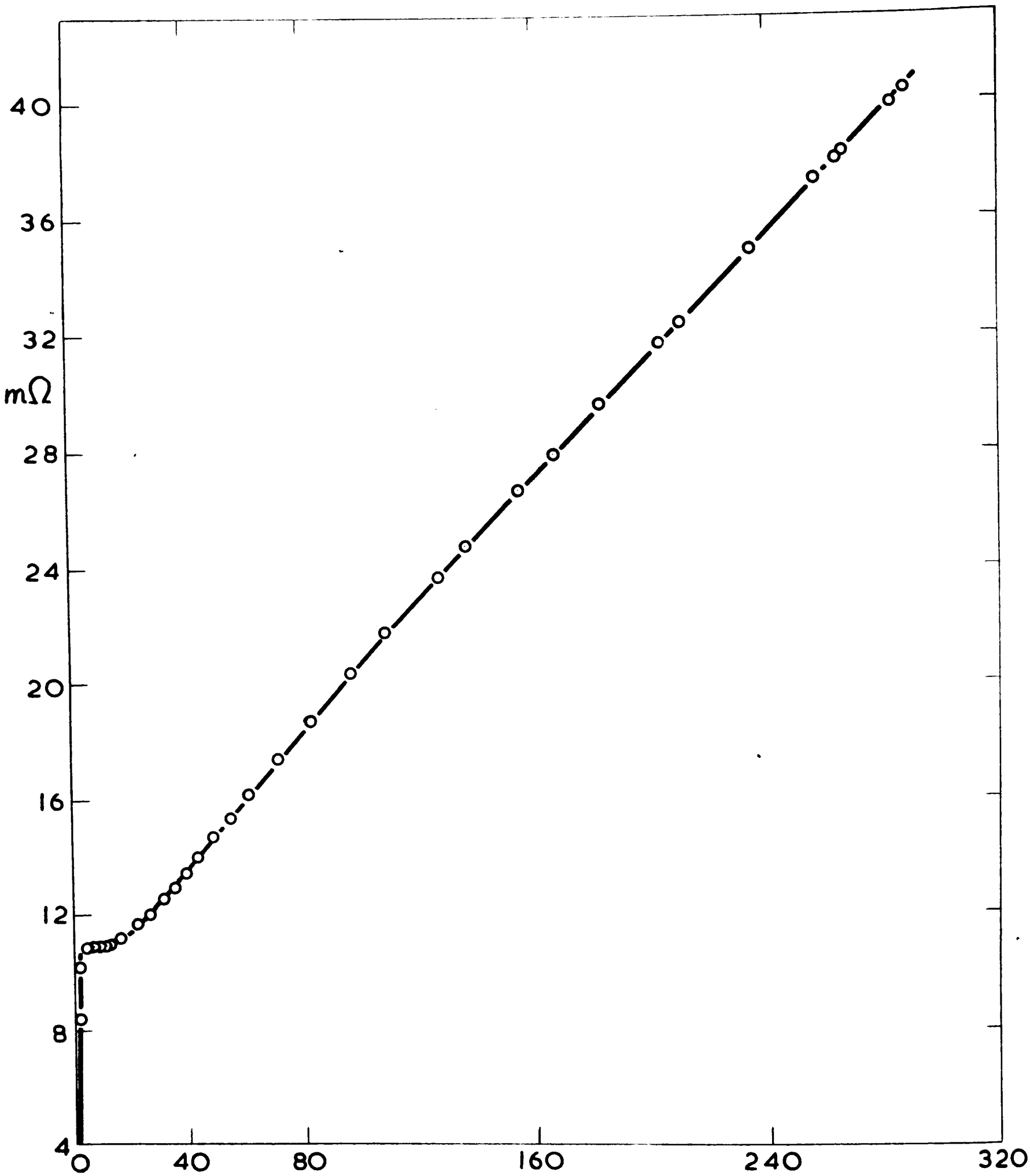
3.1. Thorium.

Low temperature resistance measurements on thorium have been reported several times in the literature, but only for a few specified temperatures. Certainly, no data from continuous runs between helium and room temperatures have been published to our knowledge.

Several specimens of thorium were obtained and investigated, firstly to check whether any low temperature anomalies existed (none, it is true, had been reported in other physical properties), and secondly to compare its

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* Some of the data presented here have been published by Lee, Meaden and Mendelssohn (1959, 1960) and Lee Meaden, Hall and King (1960).



ELECTRICAL RESISTANCE OF Th 2

FIG. 3·1

TABLE 1.

	Density	Length mm.	Diameter mm.	Source and Preparation
Th2	n.d.	37	0.380	Firth Brown (swaged)
Th4	11.68±0.03	56	1.994	A.E.R.E. (Manufacturer unknown) (probably Ca reduced)
Th5	10.09±0.02	76	1.882	Metro-Vickers Ltd. (van Arkel).

behaviour with that expected of an "ideal" metal. This we must do before we come to the abnormal transuranic elements, Np and Pu.

The α-phase of thorium, which is f.c.c., is stable from at least 18°K to 1400°C. It is a superconductor with a transition temperature at about 1.37°K (Meissner (1929), Shoenberg (1940), Wolcott and Hein (1958)). The electrical resistivity is very sensitive to impurities, especially carbon, and widely differing values have been reported. The lowest reported room temperature value is 12.2 μΩ cm (Meechan, 1955), but values exceeding 18 μΩ cm are more common. Some of the more recently published figures are given in table 2, together with Meissner and Voigt's (1930) values for comparison.

TABLE 2.

	$\mu\Omega$ cm	$\rho_{4.2}/\rho_{273}$	α 0°C. to 100
Meissner and Voigt (1930)	13 at 273	2.0%	$3.86.10^{-3}/^{\circ}C.$
Bender (1949)	24.0 at 273	-	$2.30.10^{-3}$
Weiner, Chiotti and Wilhelm (1952)	19.1 at 273	-	$3.33.10^{-3}$
Berlincourt (1959)	(1)18.9 at 297	9.09	-
	(2)17.2 at 297	5.49	-

Details of our specimens are set out in tables 1 and 3. The first specimen (Th 1) with a $\rho_{4.2}/\rho_{295}$ ratio of 36.7 was clearly very impure. It did not become superconducting even at 1.30°K. Th 4, on the other hand, had a very good density (the theoretical X-ray value is 11.72 gm. per cc) and a fairly satisfactory room temperature resistivity (19.39 $\mu\Omega$ cm). The latter specimen and also Th 5 were used in the thermoelectric power experiments (Chapter 4). Complete resistivity runs between 4°K and room temperature were done only on Th 2 and Th 5. Because of the low toxicity of Th and U, complete containment of the specimens was unnecessary, but our experiments on them were nevertheless still carried out in the cryogenic glove-box.

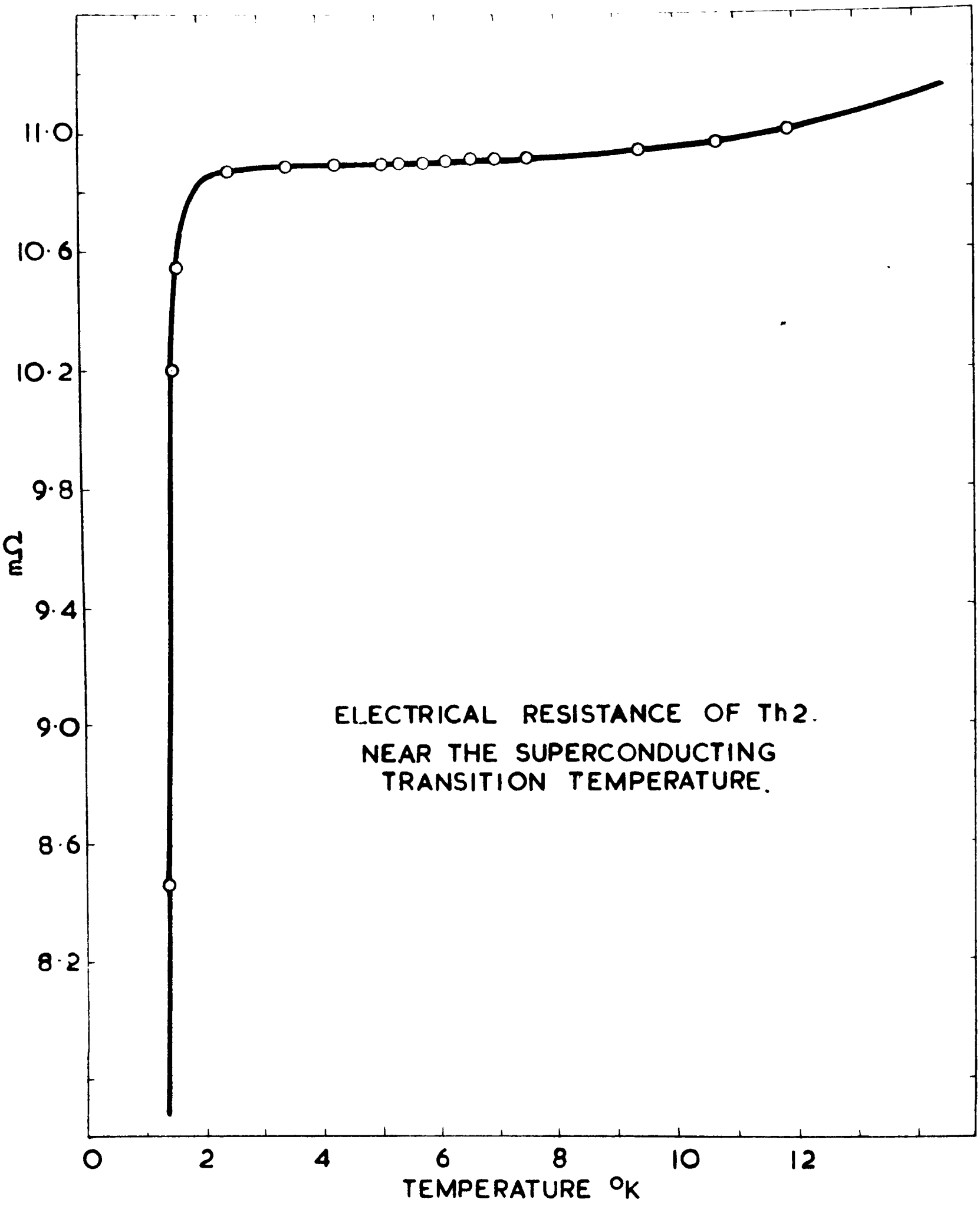

11·0
10·6
10·2
9·8
mΩ
9·4
9·0
8·6
8·2
ELECTRICAL RESISTANCE OF Th2.
NEAR THE SUPERCONDUCTING
TRANSITION TEMPERATURE.
0
2
4
6
8
10
12
TEMPERATURE °K

FIG. 3·2

Table 3.

	$\mu\Omega$ cm.	$\rho_{4.2}/\rho_{273}$	α 0 to 25°C.
Th 2	26.1±0.4 at 295	27.9%	$2.7.10^{-3}$/°C.
Th 42	24.7±0.4 at 273	-	-
Th 4	19·39 ±0· at 295		
Th 5	No abs. values, because of uncertainty in form factor.	8.54	$3.9.10^{-3}$

Th 5 was a bar of quite high purity made by the van Arkel-de Boer (iodide) process. No analysis figures were available, but figures for similar material suggested that Fe was the major impurity with probably also C and O. The specimen was used in the state in which it was received. Its density was therefore rather low, as it was not a solid rod but was rather open in structure, as a consequence of its method of manufacture. This would not affect its temperature coefficient of resistivity nor its thermo-electric power, but the absolute value of the resistivity, of course, remained unknown.

The swaged wire specimen (Th 2) would be of fairly low purity, probably containing oxide inclusions.

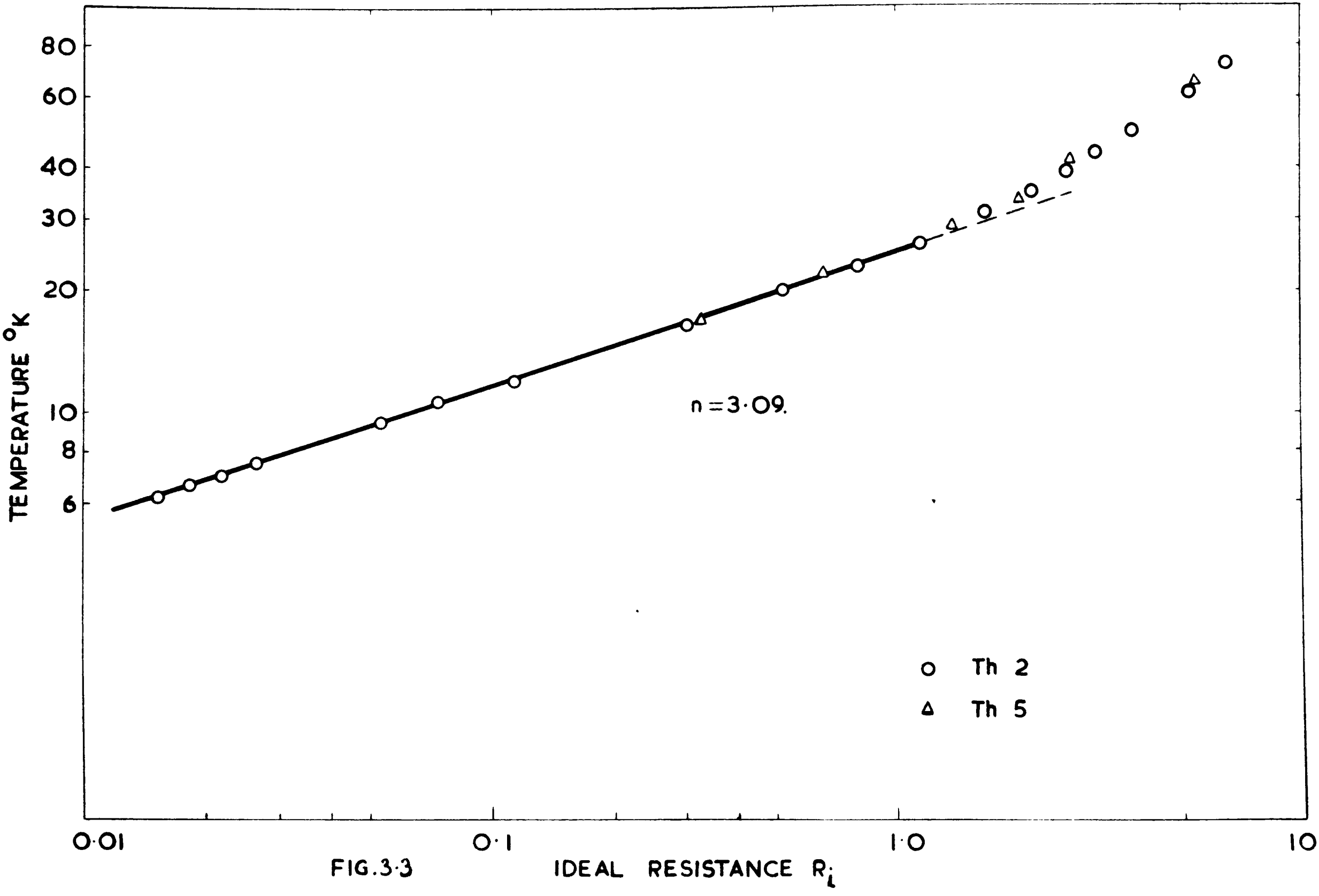

80
60
40
30
20
10
8
6
TEMPERATURE °K
n = 3·09.
Th 2
Th 5
0·01
0·1
1·0
10
IDEAL RESISTANCE R_i

FIG. 3·3

3.1.1. The results of runs on these two specimens are given in figures 3.1 to 3.4.

At the lowest temperatures attainable ($\sim 1.4^{\circ}K$) Th 2 had entered the superconducting transition region (fig. 3.2). To estimate the transition temperature T_c, the R-T curve was extrapolated to zero resistance and T_c taken as the mid-point of the nearly vertical part of the curve. The transition range ΔT_c was taken as the range over which the vertical part would have extended had there been no rounding of the curve. This indicated that the T_c was $\sim 1.35^{\circ}K$ and $\Delta T_c \sim 0.3^{\circ}K$. If, however, T_c had been defined as the temperature at which superconductivity first appeared, it would have been $\sim 1.6^{\circ}K$.

A logarithmic plot of the data on both specimens is given in fig. 3.3. Assuming that the ideal resistance R_i can be represented by the equation $R_T - R_0 = R_i = aT^n$, then the slope of the log R_i - log T plot gives n. For Th 2, n was 3.09 between 6° and $26^{\circ}K$. Data on Th 5 was unfortunately too limited for a similar graph to be drawn from which n could be determined. However, if we multiply all the data on Th 5 by the factor which normalises $(R_i)_{295}$ of Th 5 to that of Th 2, it is found that the logarithmic plots of both specimens then almost coincide. It is therefore evident that for Th 5, also, $n \sim 3$, over at least a short range of temperature.

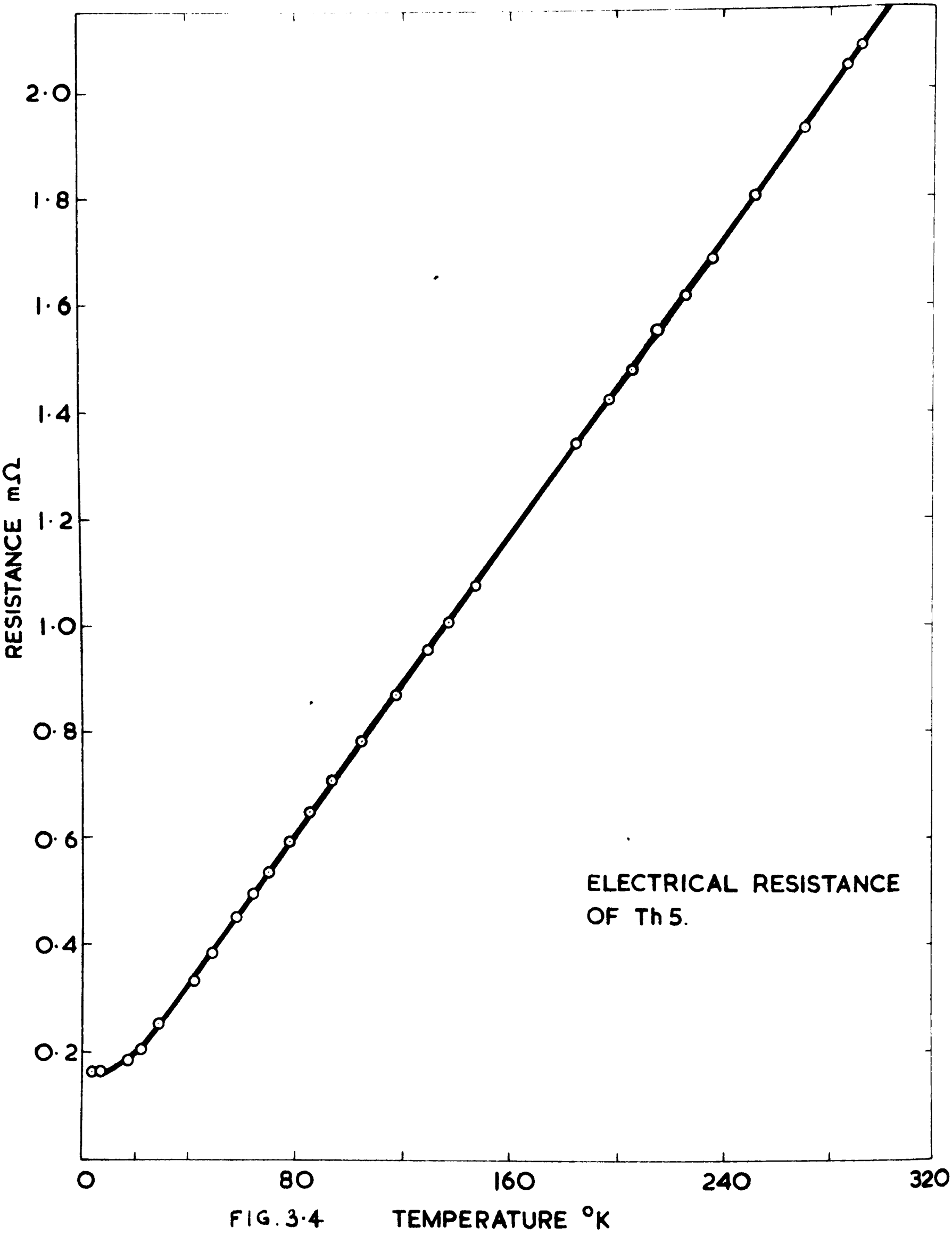

RESISTANCE mΩ
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
80
160
240
320
TEMPERATURE °K
ELECTRICAL RESISTANCE
OF Th 5.

FIG. 3·4

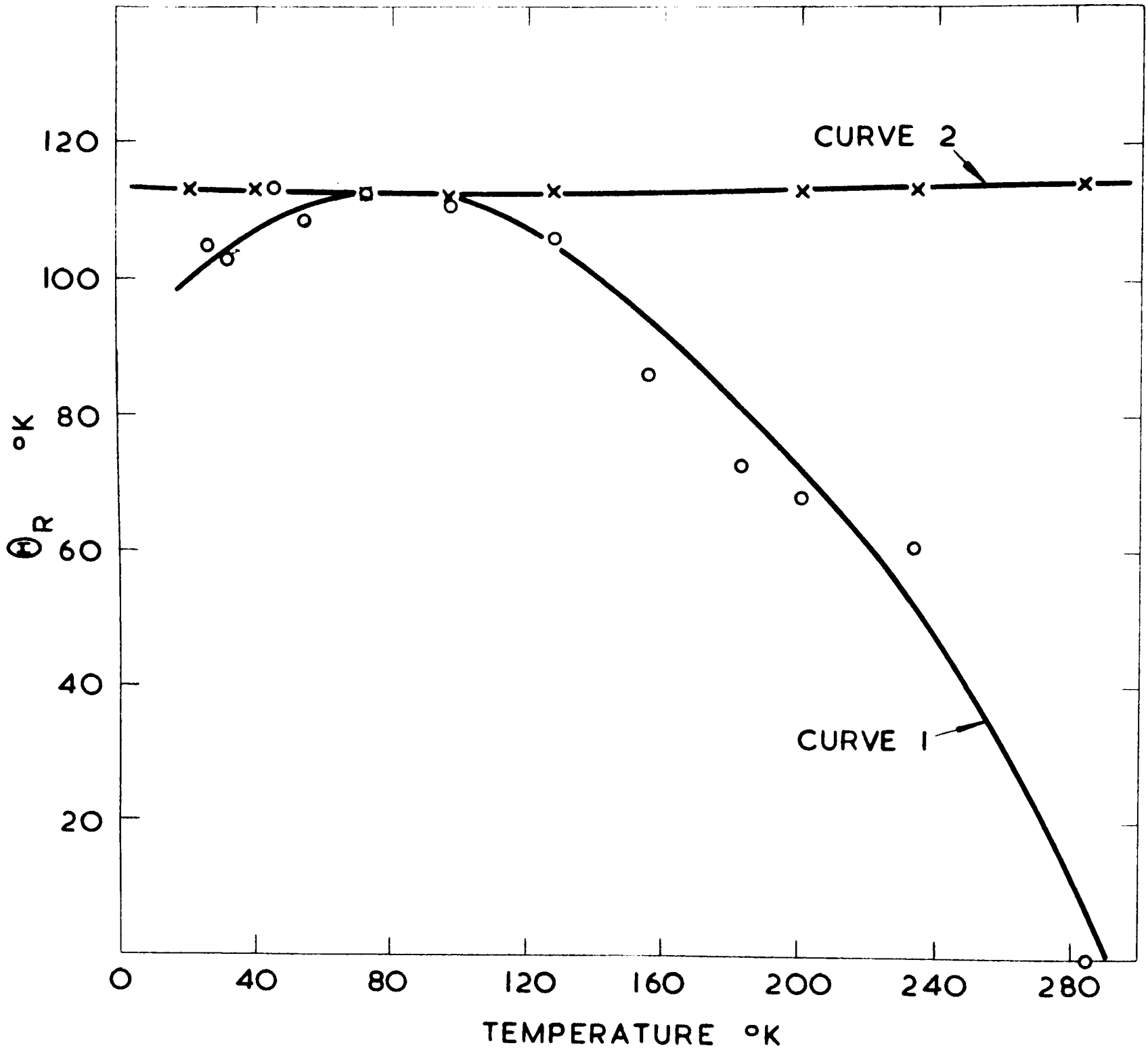
The observed resistances of the two specimens were compared with values obtained from the Grueisen-Bloch relation, eqn.(4). Since $R \propto T$ over quite a wide temperature range, a single value of Θ_R sufficed in each case.

Firstly, we see from curve 2 in fig 3.5 that the temperature dependence of Θ_R for Th 2 is indeed very slight. In fact, $\Theta_R = 113^\circ K$ is a close fit from $20^\circ K$ to the ice-point (table 4).

TABLE 4.

Comparison of Calculated and Observed values of ρ_i/ρ_θ

Th 2 with $\Theta = 113^\circ K$			Th 5 with $\Theta = 134.5^\circ K$		
Temp.	Observed	Calculated	Temp.	Observed	Calculated
$20^\circ K$	0.046	0.047			
40	0.245	0.244	$20^\circ K$	0.042	0.025
60	0.463	0.463	50	0.280	0.266
80	0.670	0.670	100	0.706	0.715
100	0.876	0.873	150	1.124	1.135
140	1.260	1.265	200	1.543	1.526
180	1.637	1.642	250	1.971	1.929
220	2.009	2.021	300	2.393	2.360
240	2.190	2.218			
273	2.499	2.527			



DEPENDENCE OF Θ_R OF THORIUM 2 ON TEMPERATURE

FIG. 3·5

With the purer Th 5, Θ_R = 134.5°K gives reasonable agreement over the range 50 to 300°K (table 4). But below 50°K, Θ begins to fall and it is necessary to assume a value of 108°K at T = 20°K to bring the calculated and observed resistances into line.

Meissner and Voigt (1930) have also determined Θ_R from resistance data at 78, 86 and 273°K. Their value of 168°K agrees little better than ours (the 134.5 of Th 5) with Θ_S derived from other physical properties. (Incidentally, we are not saying here that Θ values obtained from different sources should equal one another, but are merely making use of the fact that such Θ values, for many metals do often prove to be quite similar -(see,for example, Blackman, 1951). Such comparisons can be of particular value where, as in Np, no suitable specific heat data is available).

Wolcott and Smith (1955) have measured the specific heat of Th between 1 and 20°K, and obtained a figure of 170°K for Θ_D at the absolute zero. This value fell rapidly with increasing temperature to 138°K at 14°K, but thereafter rose slightly to 140°K at 20°K. Griffel and Skochdopole (1953) have measured the specific heat at higher temperatures, and they give Θ_D as 155°K between T = 155 and 300°K. In addition, the writer has calculated

$\Theta_E \simeq 112^\circ K$ from Einstein's formula, which relates Θ with the compressibility, and $\Theta_M \simeq 140^\circ K$ from Lindemann's melting point formula (see Mott and Jones), employing in both cases the most recent available data.

3.1.2. We will now take the opportunity of discussing the methods we employed in determining the Θ_Rs of the various metals as functions of the temperature. It is important that an author in presenting Θ_R data should specify the method(s) used, as the degree of approximation involved in the calculation often profoundly affects the results obtained. Since the accurate evaluation of the characteristic temperature from resistance data generally involves a considerable amount of labour, we have compiled a table of $\frac{d \log G}{d \log \frac{\Theta_R}{T}}$ vs. $\frac{\Theta_R}{T}$, where G is the Gruneisen function

$$\left(\frac{T}{\Theta_R}\right)^4 \int_0^{\Theta/T} \frac{z^5 dz}{(e^z-1)(1-e^{-z})},$$

thus making this task a great deal easier. This table is given in the appendix.

The calculation of Θ values in metals has been discussed by Kelly and MacDonald (1953). Making use of the Gruneisen-Bloch equation, they evaluated Θ_R from experimental results on a number of monovalent metals. Four different methods were employed, and the results obtained then compared.

The first two methods, which are quite straightforward to make use of, assume that C in the Gruneisen-Bloch equation $\left[\rho_i = \frac{C}{\Theta_R} \left(\frac{T}{\Theta_R} \right) G \left(\frac{\Theta_R}{T} \right) \right]$ is approximately constant over quite a wide temperature range, but unfortunately both then require a reference temperature, which must be taken in a region where Θ_R is already known to be essentially constant. The effect of the choice of this reference temperature is quite critical. This was overcome in the other methods by determining the quantity $\frac{d\rho/dT}{\rho/T}$ at every temperature. These methods are more involved but, being more accurate, were used in the present work. The procedure was as follows:

Taking logarithms of the Gruneisen-Bloch equation and differentiating with respect to log T, we obtain

$$\frac{d \log \rho}{d \log T} = 1 + \frac{d \log G}{d \log T} - 2 \frac{d \log \Theta_R}{d \log T}$$

$$= 1 + \left\{ \frac{d \log G}{d \log \Theta_R/T} \left(\frac{d \log \Theta_R}{d \log T} - 1 \right) \right\} - 2 \frac{d \log \Theta_R}{d \log T}$$

$$\frac{d \log \rho}{d \log T} = 1 + \left| \frac{d \log G}{d \log \Theta_R/T} \right| - \frac{d \log \Theta_R}{d \log T} \left(2 + \left| \frac{d \log G}{d \log \Theta_R/T} \right| \right) \qquad \ldots(12)$$

If Θ_R is constant, this reduces to

$$\frac{d \log \rho}{d \log T} = 1 + \left| \frac{d \log G}{d \log \Theta_R/T} \right| \qquad \ldots(13)$$

Graphs of $\log_{10} \frac{\Theta_R}{T}$ vs. $\log_{10} G$ were plotted on a very large scale on ordinary graph paper ($G(\frac{\Theta_R}{T})$ as a function of $\frac{\Theta_R}{T}$ is given in Gruneisen (1933) and MacDonald (1956)). Slopes were then obtained from these graphs for various $\frac{\Theta_R}{T}$. Large scale graphs of $\frac{d \log G}{d \log \Theta_R/T}$ as a function of $\frac{\Theta_R}{T}$ were next plotted and smooth curves drawn. From these the table given on p.145 was compiled.

Using this table, Θ_R/T can now be obtained at once by means of equation (13), as $\frac{d \log \rho}{d \log T}$ is known from experimental observations. Θ_R as a function of T is thus obtained approximately. We can now make use of the more accurate equation (12), starting from a region in which Θ_R has been found to be almost constant; for then the correction term in (12) is small, and accurate Θ_Rs can be obtained quickly by successive approximation.

The result of applying these methods on Th 2 is shown in fig. 3.5. Firstly, curve 1 was obtained, using the approximate equation (13). Since Θ_R was nearly constant over the temperature range 50 to 100°K, this region was taken as the starting point for the application of the correction term in (12). By this means, the more accurate curve 2 was obtained.

3.2. Uranium.

Two samples of uranium were investigated. The first sample, U1, obtained from A.E.R.E., was stated to be "pure",

TABLE 5.

	Density	Length mm.	Diam. mm.	Source	Description
U1	n.d	50	0.890	A.E.R.E	Uniform wire, as recd.
U2	19.05 ±0.02	26.5	~1mm. sq.	U.S.A.E.C	H.P. electrolytic U: machined and cut into rod (sq. + section)
U2b	19.05 ±0.01	56.5	~ 4	do	do. (circular + section).

but no purity analysis figures were available. The second sample was electrolytic uranium of the highest purity, prepared by the Blumenthal technique. Spectrographic and chemical analysis figures are given below. The specimens were machined to shape, rather than cast, in order to retain their original purity. U2 was used for the electrical resistivity experiments and U2b for the thermoelectric power experiments. The isotropy of these specimens is likely to have been very good, since resistivity measurements on other samples from the same bar before and after β-quenching showed good agreement.

3.2.1. Uranium has three crystallographic modifications, and the orthorhombic room temperature phase is stable up

TABLE 6.

Composition of High Purity Uranium (bar HPX 131)

Chemical Analysis			Spec. Analysis.		
C	N	O	K	Li	Si
12	18	49ppm	100	40	10ppm

Not detected: Be <0.5, Cu <1, Na <10, Sb <1, Ag <1, Bi <1, Fe <2, Ni <5, Sn <5, Al <5, Ca <20, Mg <1, P <50, Ti <50, As <10, Co <5, Mn <1, Pb <1, Zn <50, B <0.1, Cr <1, Mo <20

Isotopic Analysis: U^{238} 99.595±0.004, U^{235} 0.405±0.004.

TABLE 7.

Authors	T_c*	ΔT_c	Method
Aschermann and Justi (1942)	1.3°K	-	Resistance
Alekseyevsky and Mitunov (1947)	1.3°K	-	Ballistic M.I.
Goodman and Shoenberg (1950)	1) ~1.3 2) ~0.75	~0.2 ~0.2	" "
Kilpatrick, Hammel and Mapother (1955)	1) 0.77 2) 0.80	0.2-0.3	" "
Hein, Henry and Wolcott (1957)	1) 0.35 2) 0.39	0.45	" "
Present Work { H1	0.86±0.05	0.2	Resistance
Present Work { H2	<1.45	-	"

* T_c is defined as the temperature at which half the metal has become superconducting (as Shoenberg: p.223 of Superconductivity

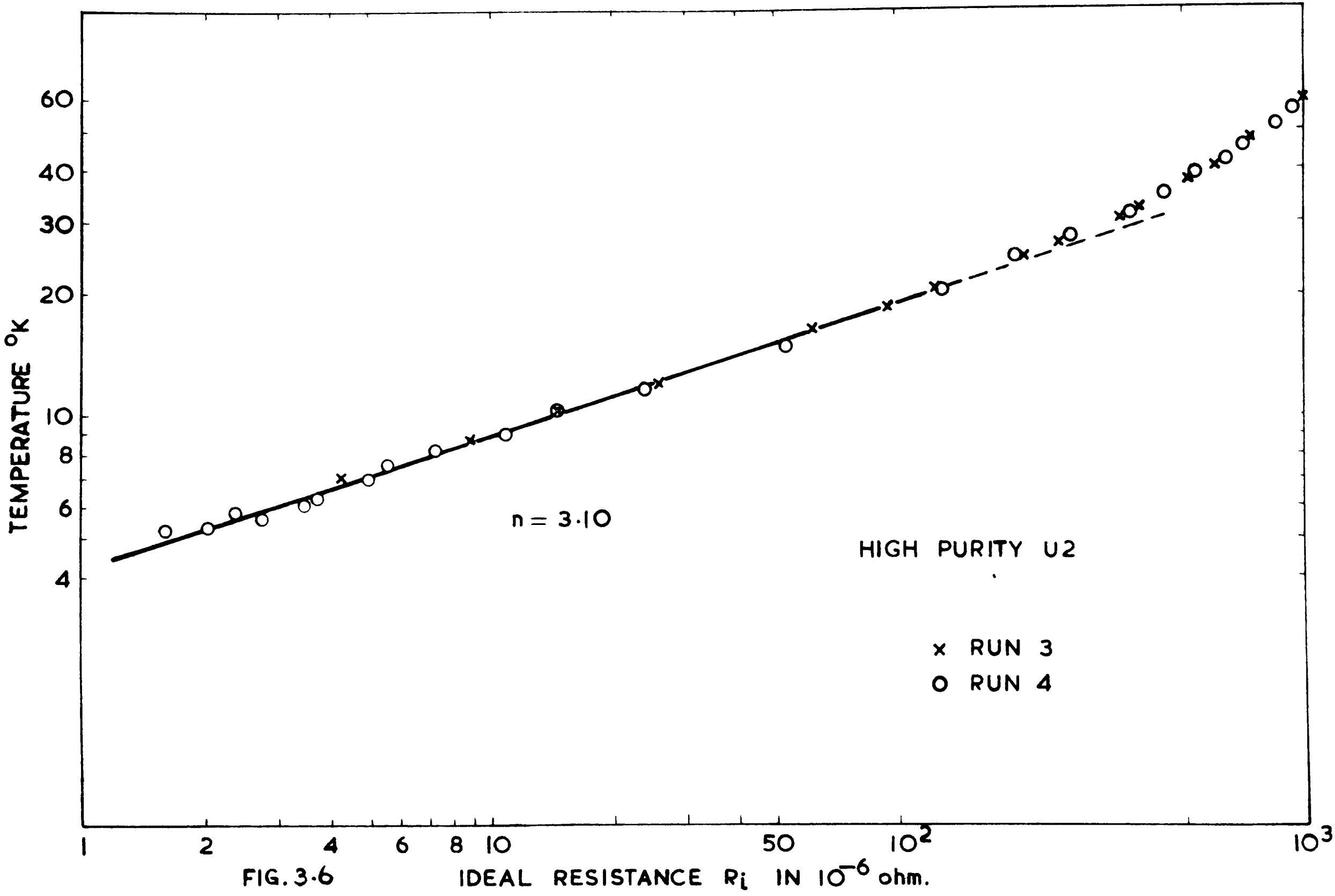

TEMPERATURE °K
60
40
30
20
10
8
6
4
n = 3·10
HIGH PURITY U2
x RUN 3
O RUN 4
1
2
4
6
8
10
50
10²
10³
IDEAL RESISTANCE Ri IN 10⁻⁶ ohm.

FIG. 3·6

to 668°C. It is known to be a superconductor, but values for its transition temperature have varied considerably (table 7).

Our first specimen U1 was found to have a transition temperature at 0.86°K with a transition width of 0.2°K. (T_c and ΔT_c were defined in section 3.1.1. However, if T_c is taken as the temperature at which superconductivity first appears, then it would be 0.97°K ±0.05). The resistance of U1 had, at 0.75°K, fallen to 1/2000 of that at 4.2°K.

The work on U1 was done in Oxford, but that on U2 was carried out in the plutonium cryostat at A.E.R.E.

TABLE 8.

Author	ρ_T	$\rho_{4.2}$	$\rho_{4.2}/\rho_{273}$	α (0to25°C)
Chandrasekhar and Hulm (1958)	29.09 at 298	3.86	~13.3	-
Berlincourt (1959)	1) 34.0 at 300	4.8	15.4	$\sim 3.3.10^{-3}$
	2) 29.7 at 273	4.43	8.3	-
	3) 25.5-39.4 at 300 (single crystal)	-	3.4-4.4	-
Present Work U1	33.1±0.1 at 295	4.8	15.4	$2.79.10^{-3}$
U2	30.78±0.1at 295	0.99	3.45	$3.06_3 10^{-3}$ /°K

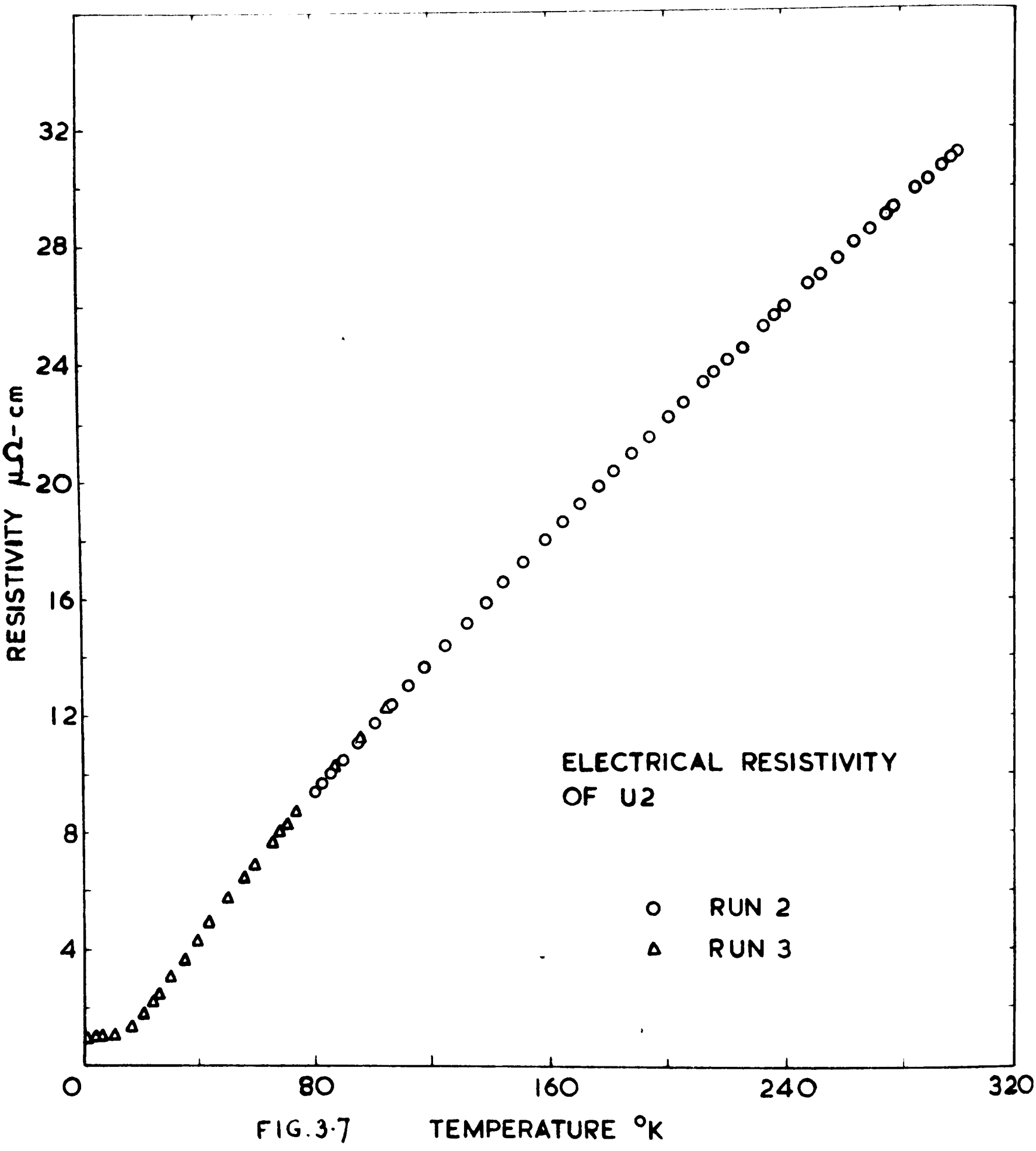

RESISTIVITY μΩ-cm
32
28
24
20
16
12
8
4
0
80
160
240
320
ELECTRICAL RESISTIVITY
OF U2
RUN 2
RUN 3
TEMPERATURE °K

FIG. 3·7

At that time the lowest temperature that could be reached was only 1.45°K, but evidence could be seen at this temperature of the commencement of a very wide transition. It would appear then that this purer specimen had a higher transition temperature and, possibly larger width, than the less pure specimen.

Two runs on U2 were done at low temperatures and a logarithmic plot of the ideal resistance is given in fig. 3.6. It is seen that the power index of n over the range 5° to 21°K is 3.10, almost the same as that of thorium.

The variation of the resistivity with temperature between 1.5 and 300°K is shown in fig. 3.7. It will be observed that at the higher temperatures, and contrary to the behaviour of most metals, R is not strictly proportional to T, but increases rather less rapidly than T. This phenomenon occurs fairly widely in the transition metals at high temperatures, and we shall discuss this later in section 5.3. It will be seen shortly that the effect is of still greater magnitude in neptunium (section 3.3.1).

In such a metal, a comparison with the Gruneisen-Bloch relation is not very rewarding. Θ_R decreases monotonically with increasing temperature from a value of 101°K at T = 20°K to about 60°K at room temperature, due to

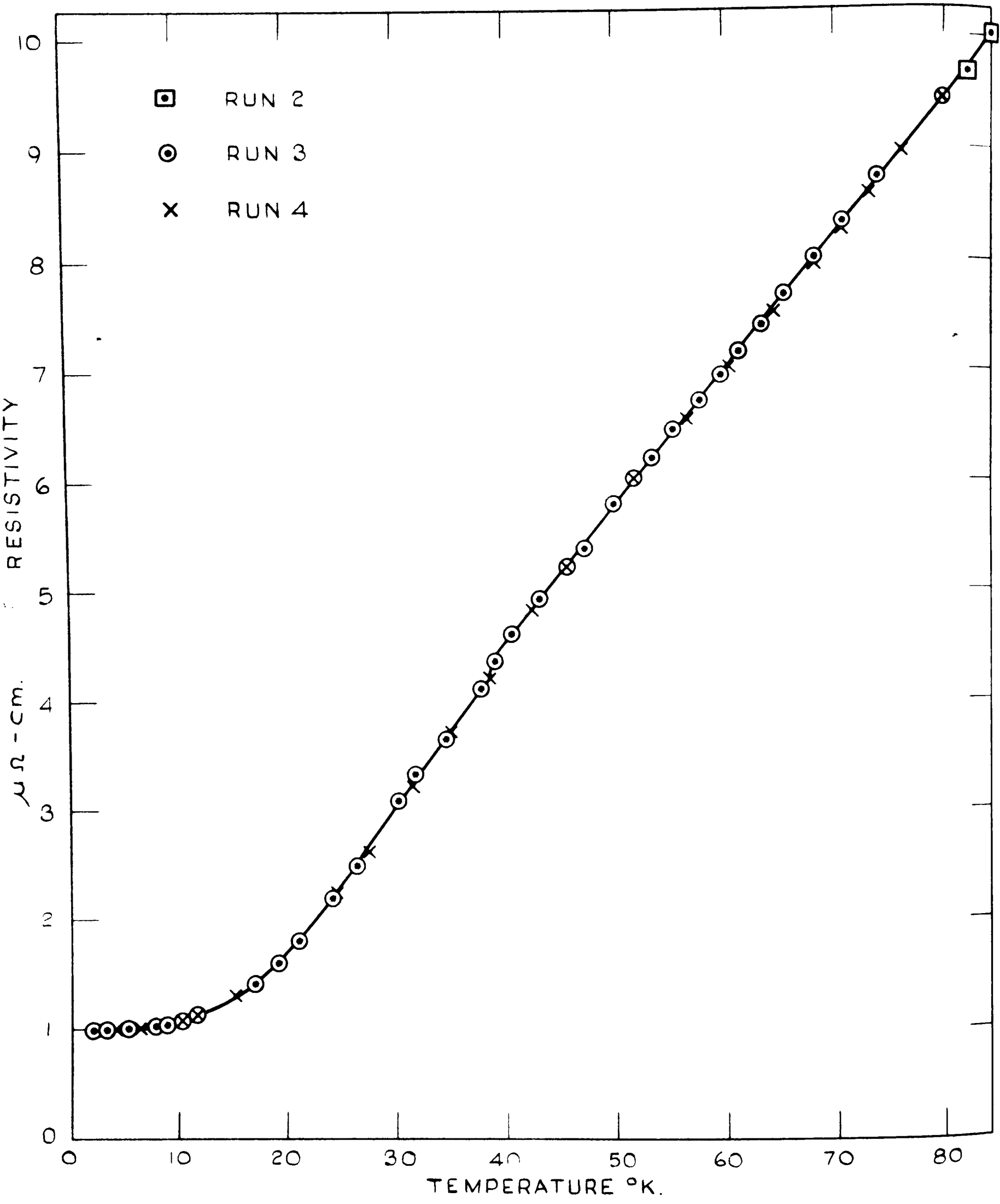


FIG. 3.8 ELECTRICAL RESISTIVITY OF U2.

the failure of the $\rho \propto T$ law. Θ_S derived by other means are considerably higher. For example, we obtain 154°K from the elastic constants and 142 from Einstein's formula. Smith and Wolcott's (1955) specific heat data lead to Θ_D = 200°K at the absolute zero and 170 at T = 20°K, while Gordon, Jones and Long (1952) obtained Θ_D = 162 between T = 15 and 300°K. We see then that in U, and to a lesser extent in Th, Θ_S derived from our resistance data are lower than those obtained from the specific heats.

3.2.2. A small step anomaly in the electrical resistivity of U2 was observed at ~39°K in the first low temperature run (run 3 - see fig. 3.8). While the step itself was little larger than the experimental scatter of the data, there did appear to be quite a definite change in slope as well. Precisely the same path was followed during the next run. The anomaly is small and this evidence by itself is by no means decisive. However, a search of the literature revealed further peculiarities in other physical properties at roughly the same temperature.

Most important of these is Berlincourt's (1959) work on the temperature dependence of the Hall coefficient. In both his specimens he found a remarkable fall in the magnitude of the Hall coefficient (fig. 3.9), commencing at 35 to 40°K on cooling, and commented that this was

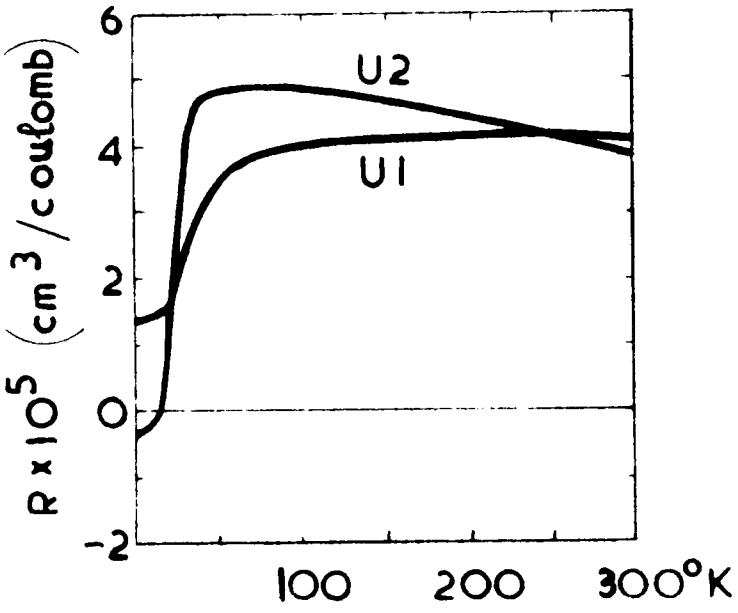


FIG 3·9 HALL COEFFICIENT vs. TEMPERATURE
FOR TWO SPECIMENS OF URANIUM (BERLINCOURT 1959)
U2 WAS THE PURER.

suggestive of a phase transformation. He carried out electrical resistivity measurements, but was unable to find any support for this suggestion. Now Tyler, Wilson and Wolga (1952) had found that the thermoelectric power of uranium displayed a minimum at about 40°K. We therefore thought it advisable to measure the thermoelectric power of a specimen, made of the same material as that which showed the resistivity anomaly. The results on this specimen, U2b, are fully presented in section 4.3, but we will say at once that a change in slope at ~40°K was in fact found (fig. 4.4). No low temperature work (below 80°K) on the magnetic susceptibility appears to have been done, but the specific heat has been measured (Jones, Gordon and Long, 1952) though without observing any unusual behaviour. It might be remarked that their experimental points near 40°K, which came at 31.2, 35.3, 40.1, 45.3°K, were rather widely spaced, so that a small or narrow peak could perhaps have been missed.

Lastly, two other peculiarities should be mentioned but, since they manifest themselves at rather higher temperatures, they probably bear no relation to our discussion, though they may possibly be related to one another. Both Schuch and Laquer (1952) and Bijl and

Pullan (see Rosenberg, 1955) found a change in sign of the thermal expansion coefficient near 60°K and that between 60 and 20°K the sign was negative; while Rosenberg (1955) found there was an appreciable contribution to the thermal conductivity from the lattice at temperatures above 60°K. Schuch and Laquer's work is not explicable by preferred orientation at any rate, since they used rods of varying orientation in their dilatometry. Moreover, confirmation comes on a microscopic scale from X-ray diffractometry by Bridge, Schwartz and Vaughan (1956), who found an expansion of the a-axis below ≈ 60°K.

On account of the correspondence with the abnormal behaviour in the Hall coefficient and the thermoelectric power at 40°K, described above, we believe the anomaly in the electrical resistivity to be almost certainly genuine; and we suggest that the effect is due to a fundamental property of the metal, rather than being merely an impurity effect, such as in the alkali metals at low temperatures (MacDonald and Mendelssohn, 1950). Possibly, Berlincourt with his less pure uranium (as evidenced by resistivity ratios) did not observe the resistivity anomaly because of the masking effect of additional impurities.

One explanation of the phenomenon (suggested by

Berlincourt) is that it is due to the occurrence of a solid-state phase transformation. Transformations at such low temperatures have been found in several elements, notably sodium and lithium (Barrett, 1956), not to mention cerium (James, Legvold and Spedding, 1952). However, no time effects at low temperatures, that would be suggestive of a sluggish transformation, were observed. Furthermore, Bridge, Schwartz and Vaughan (1956) found that, in their specimen at least, the X-ray diffraction pattern at 20°K was still that of orthorhombic α-uranium.

The available evidence is really too limited at present for any conclusions to be safely drawn. We feel that further X-ray diffraction work (and perhaps neutron diffraction also) should be done, since Bridge et al's measurements were limited to only one reading (at 20°K) below 63°K. Such diffraction experiments might well hold the key to the problem.

3.3. Neptunium.

The available neptunium metal was part of a small quantity prepared in 1957 at Windscale from the residues of the plutonium extraction plant by a bomb reduction process (Nairn, Collins, McKay and Maddock, 1958).

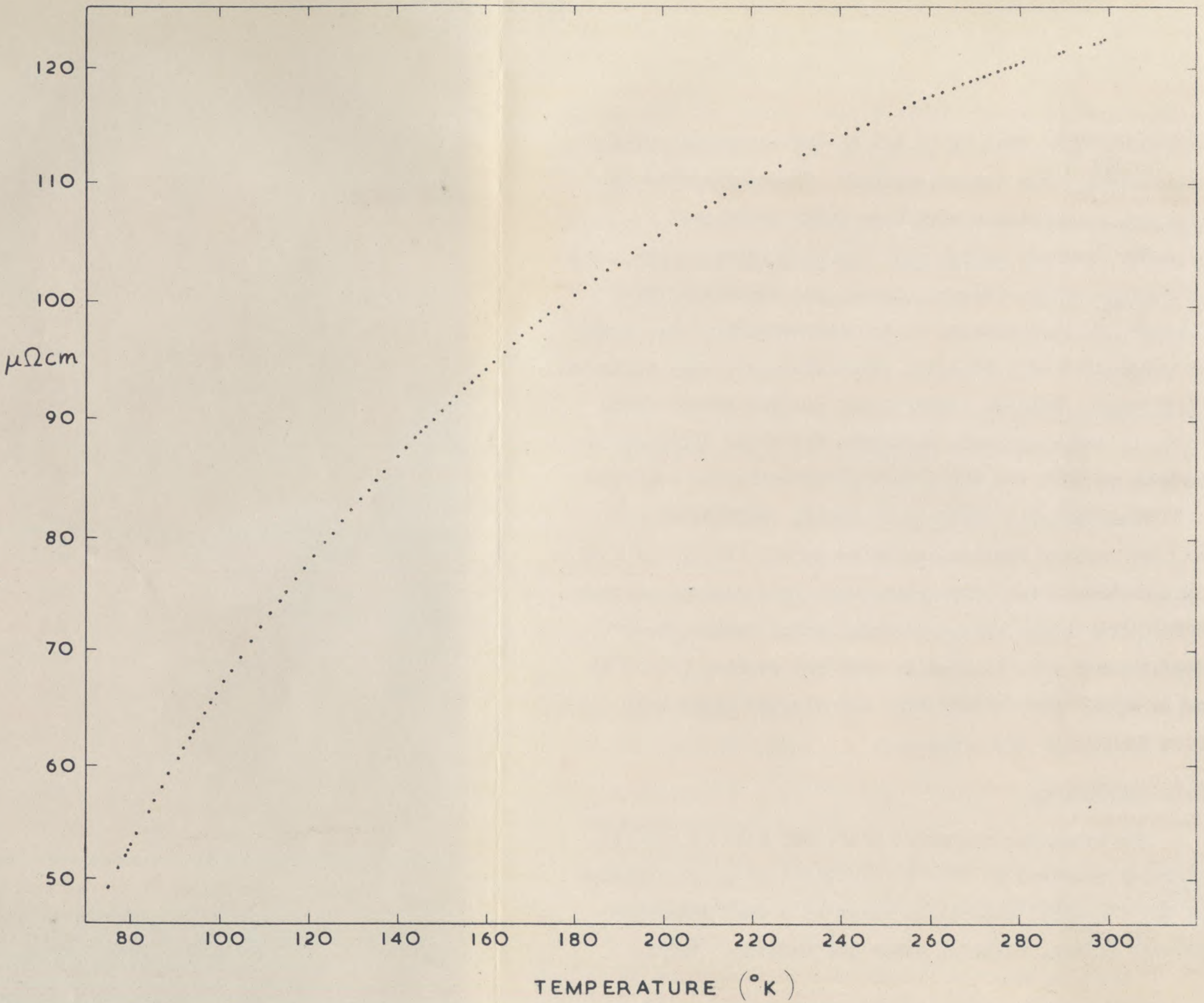


FIG. 3.10. ELECTRICAL RESISTIVITY OF Np I RUN I.

TABLE 9.

Density	Length mm.	Diam. mm.	Description
Np 1 20.25 ±0.02	28	2.170	Cast in precision-bore silica tube, and later well-annealed.
Np 2 20.14 ±0.02	14	~4	Arc-melted into elongated globule.
Np 3 20.5 ±0.2	15	~1.0	Np 2 was re-arc-melted and then extruded.

Certain physical properties of this material were studied at once at A.E.R.E., Harwell. These were the specific heat above room temperature (Evans and Mardon, 1959), the allotropic transformations (Lee, Mardon, Pearce and Hall, 1959) and the electrical resistivity and thermoelectric power between 300 and 900°K (Lee, Evans, Hall and King, 1959). The specimen employed in the last of these investigations was the identical one later used by us (our number, Np 1) for a study of the electrical resistivity below room temperature. Np 2 was also used in our study of the resistivity, while Np 3 was our specimen for the thermoelectric power experiments.

The purity of the original reduction billet, 99 weight per cent, was not high by ordinary standards. The

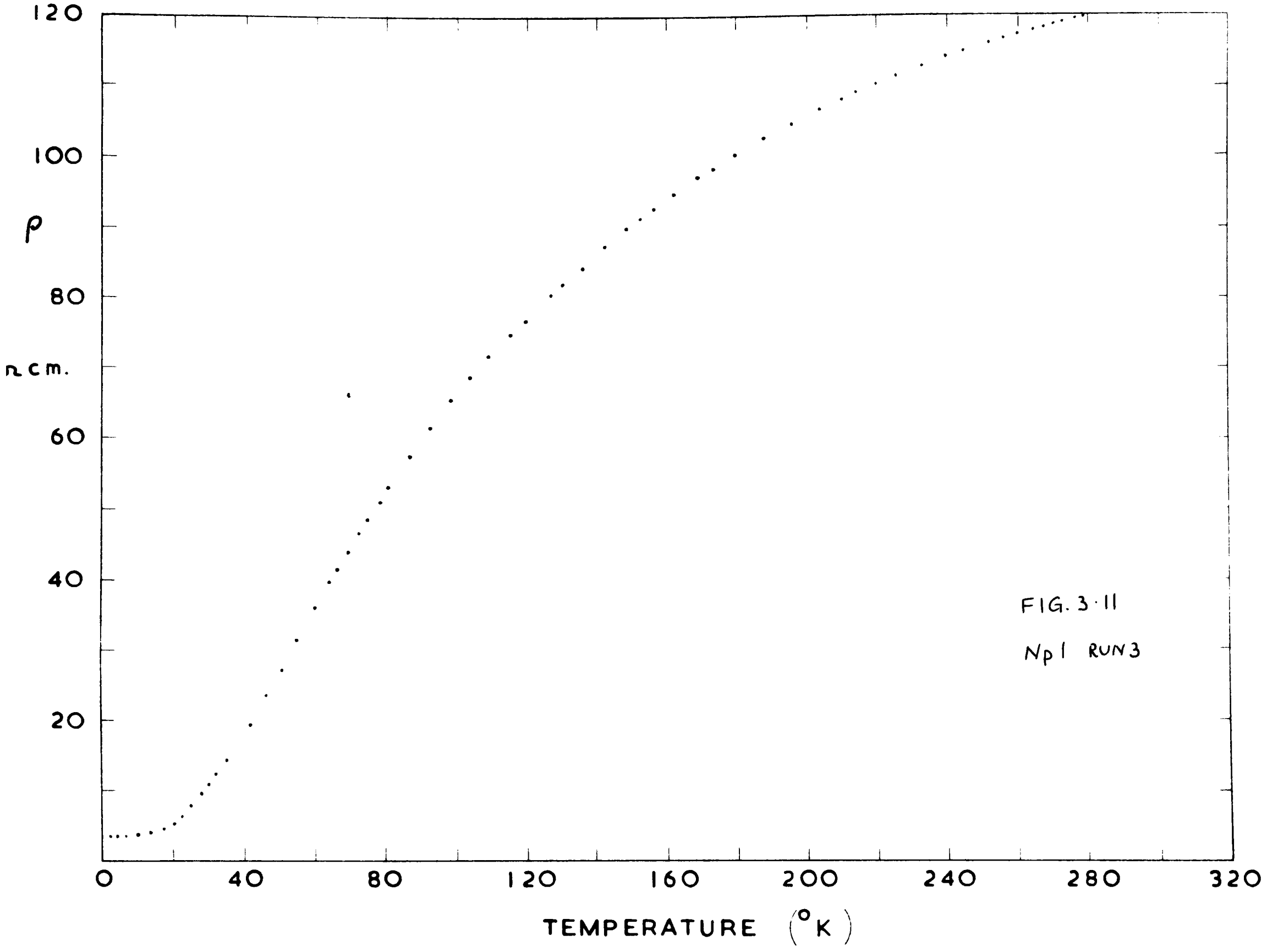


FIG. 3·11. ELECTRICAL RESISTIVITY OF Np I RUN 3

principal impurities in % were given as

Ca	0.34	U	0.22	Ni	0.06	Mg	0.03
Cr	0.03	Pu	0.03	Al	0.02	V	> 0.06
						Mo	> 0.05

Figures for fluorine and oxygen, which were probably also present, were not obtained. Since most of the above elements are very much lighter than Np, the impurity content in atomic per cent would be as much as 4 or 5. Fortunately, it is likely that the Ca and Mg content was much reduced by the arc-melting during the preparation of the samples.

The densities of all the specimens were high, and in good agreement with the theoretical value of 20.45 gm per cc.

3.3.1. The first experiments on Np 1 were carried out in Oxford. For this purpose the specimen was enclosed in a sealed cylindrical can, in the manner described in section 2.2, and its electrical resistance measured down to 0.75°K. The specimen did not become superconducting, but there were indications that the resistance, which had been constant at 3.55 microhm-cm since T = 4.2°K, was just beginning to fall again, as though the onset of superconductivity was imminent. A T_c below 0.75°K in Np is not too unlikely, since both Th and U are superconductors with low transition temperatures. One should remember

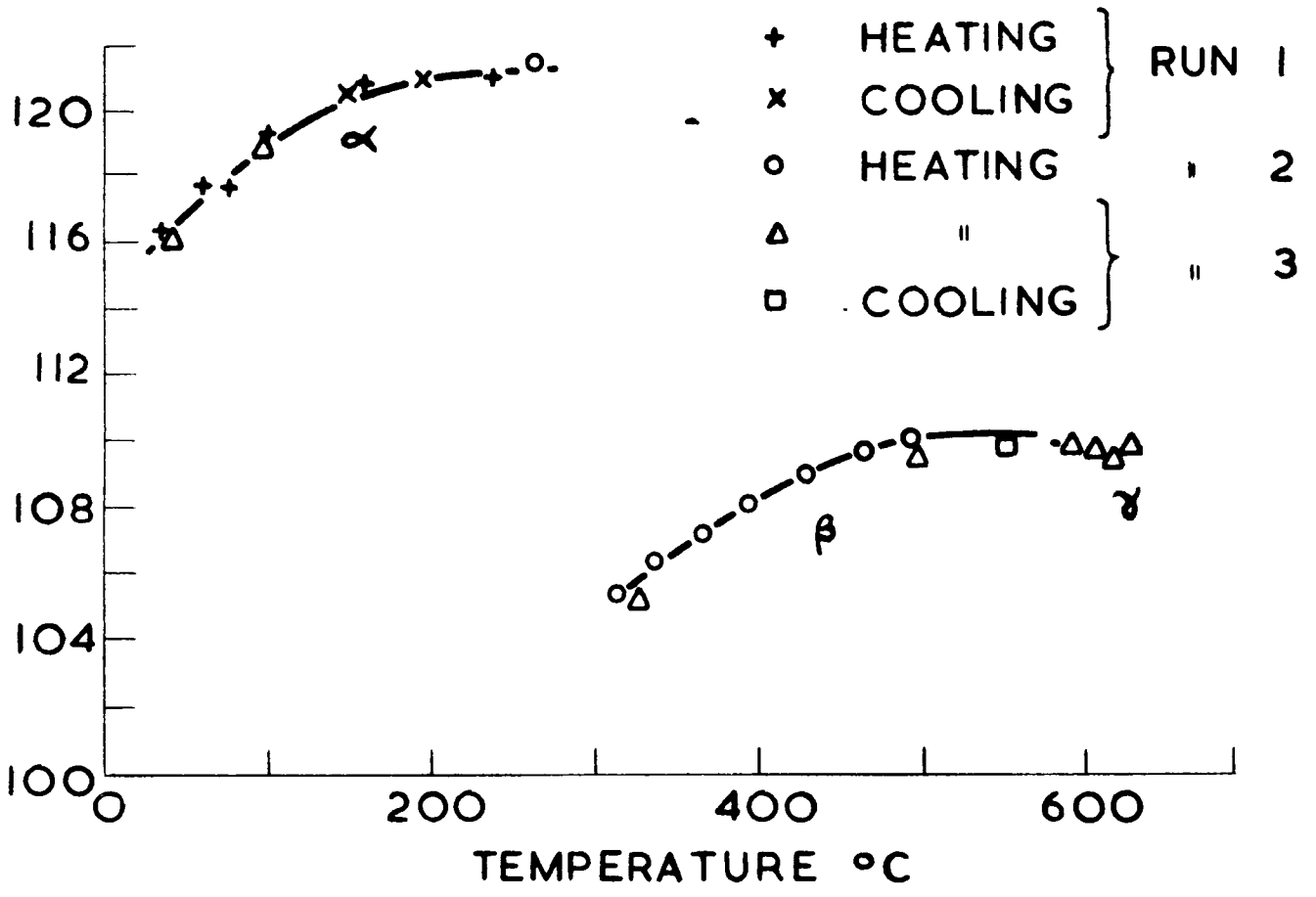


FIG. 3.12 ELECTRICAL RESISTIVITY OF NEPTUNIUM
(FROM LEE, EVANS, HALL AND KING, 1959)

that our Np sample contained 0.22 $^{w}/_{o}$ (and therefore approximately 0.22 $^{a}/_{o}$) of U, and this could, perhaps, account for the slight signs of superconductivity. To resolve this question, Np should be taken to still lower temperatures and a ballistic mutual inductance method employed, since a determination of the magnetic moment gives a direct measure of the fraction which is superconducting.

All the remaining experiments on Np were carried out using the active cryostat at A.E.R.E.

Considering first the relationship between electrical resistivity and temperature in figs. 3.10 and 3.11, two points of interest are immediately apparent. These are the extremely high value of the resistivity at room temperature, which is four times greater than that of uranium and fifteen times that of a transition element such as iron, and the monotonically decreasing value of the temperature coefficient above 60°K. As can be seen from fig. 3.12 (Lee, Evans et al, 1959), the latter continues decreasing right up to the α-β phase change at 550°K, by which time it has become almost zero. This phenomenon will be discussed in sections 5.3 and 5.4. Values for the resistivity and the rate of change of resistivity with temperature are tabulated in Table 10.

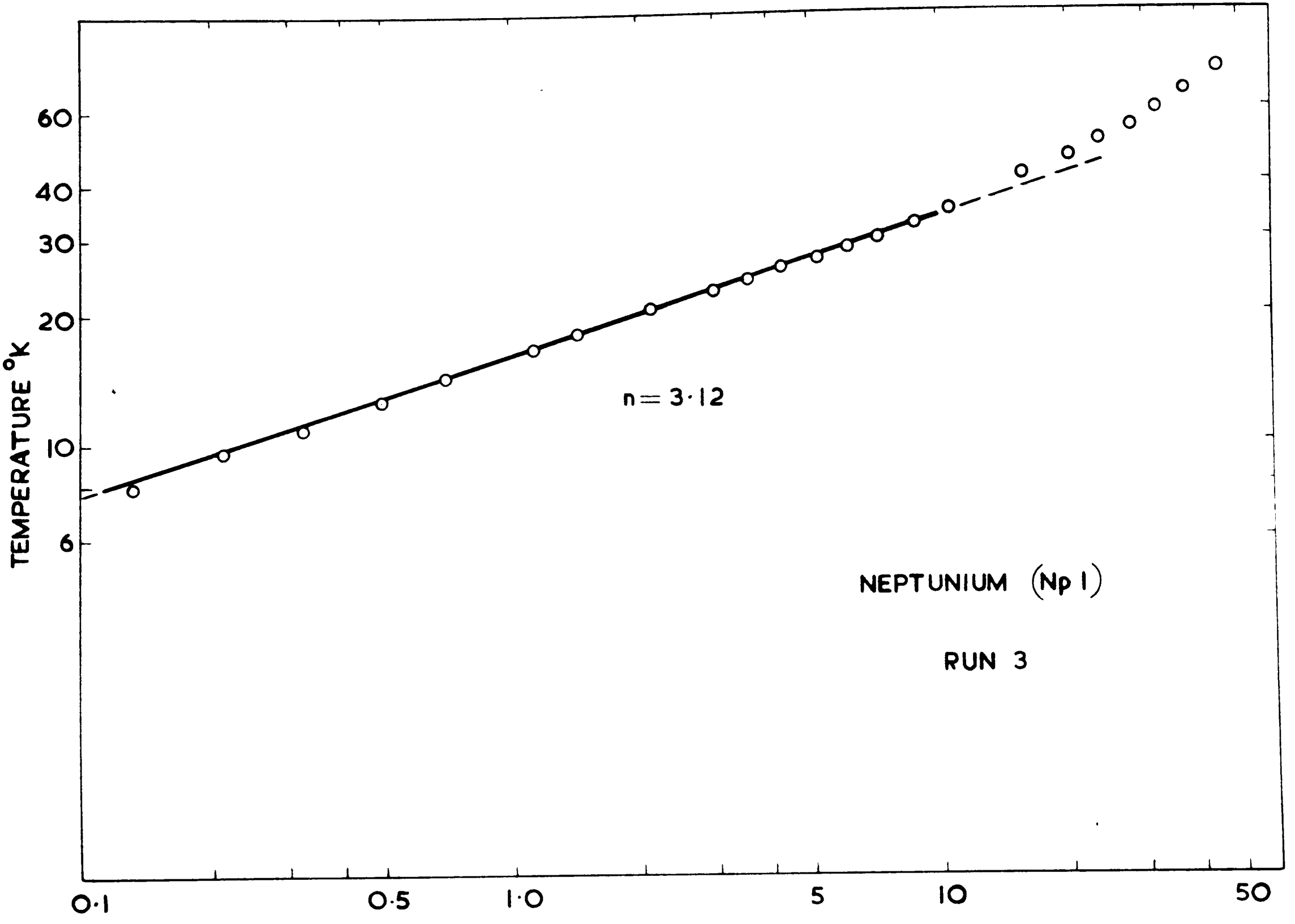


FIG. 3·13 IDEAL RESISTIVITY R_i $\mu\Omega$–cm

TABLE 10.

Temperature	Resistivity	$d\rho/dT$
4.2°K	3.55μΩcm	0
20	5.5	0.40μΩcm/°K
40	18.9	0.84
50	27.5	0.90
60	36.8	0.89
80	53.5	0.74
100	66.7	0.61
150	90.8	0.40
200	106.1	0.25
250	116.2	0.15
300	122.3±0.2	0.085

As explained in section 2.10, these figures are not corrected for thermal expansion.

When the ρ_i vs. T data at low temperatures are plotted logarithmically (fig. 3.13), we find that the power index of T is 3.12 between 8° and 32°K. As with Th (n = 3.09) and U (3.10), the uncertainty associated with deciding on the exact line to draw introduces an error of 0.05 at most. We may thus say that for these

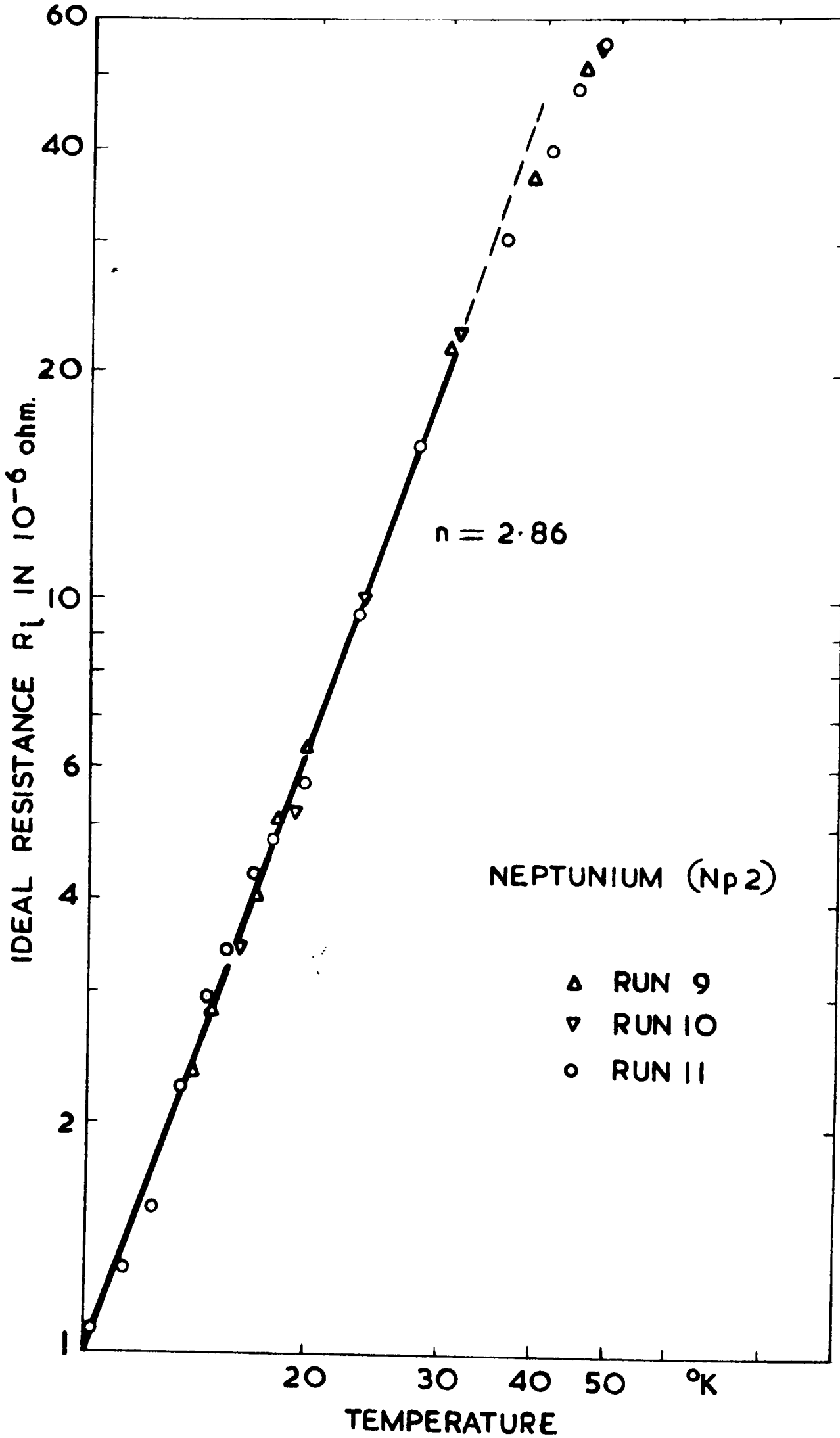

60
40
20
10
6
4
2
1
IDEAL RESISTANCE R_i IN 10^{-6} ohm.
n = 2·86
NEPTUNIUM (Np 2)
RUN 9
RUN 10
RUN 11
20
30
40
50
°K
TEMPERATURE

FIG. 3·14

specimens n is 3.1±0.05*. The power indices of the transition elements commonly lie between 3 and 5, but, as discussed in Chapter 1, no full qualitative explanation of the R-T behaviour of these metals at low temperatures has yet been given. One attempt was made by Wilson (1938), who obtained a relationship for the resistive contribution from s-d scattering which, in one approximation, leads to $\rho_i \propto T^3$. Experimentally it is found that the temperature variation of some transition metals tends towards T^2 at the lowest temperatures ($< 10^{\circ}K$) (White and Woods, 1959). This has been attributed to electron-electron interactions by Baber (1937). Our data did not really allow an accurate determination of n below $\sim 10^{\circ}K$ on our specimens.

As in the case of uranium, little can be learnt from a comparison of the data on neptunium with the Gruneisen-Bloch equation. $\Theta_R = 137^{\circ}K$ is an approximate fit between $T = 17$ and $35^{\circ}K$, and, if this value is taken for the computation, fig. 3.15 is obtained. On the other hand, if Θ_R is determined as a function of T, we find that Θ_R simply decreases steadily, being about 135 at $T = 35^{\circ}K$, 92 at $80^{\circ}K$ and 70 at $120^{\circ}K$, for example. Below $T = 17^{\circ}K$ also, Θ_R appears to fall off slightly.

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*A second specimen of Np, described in the next section, had $n = 2.86 \pm 0.1$. Data are shown in fig. 3.14.

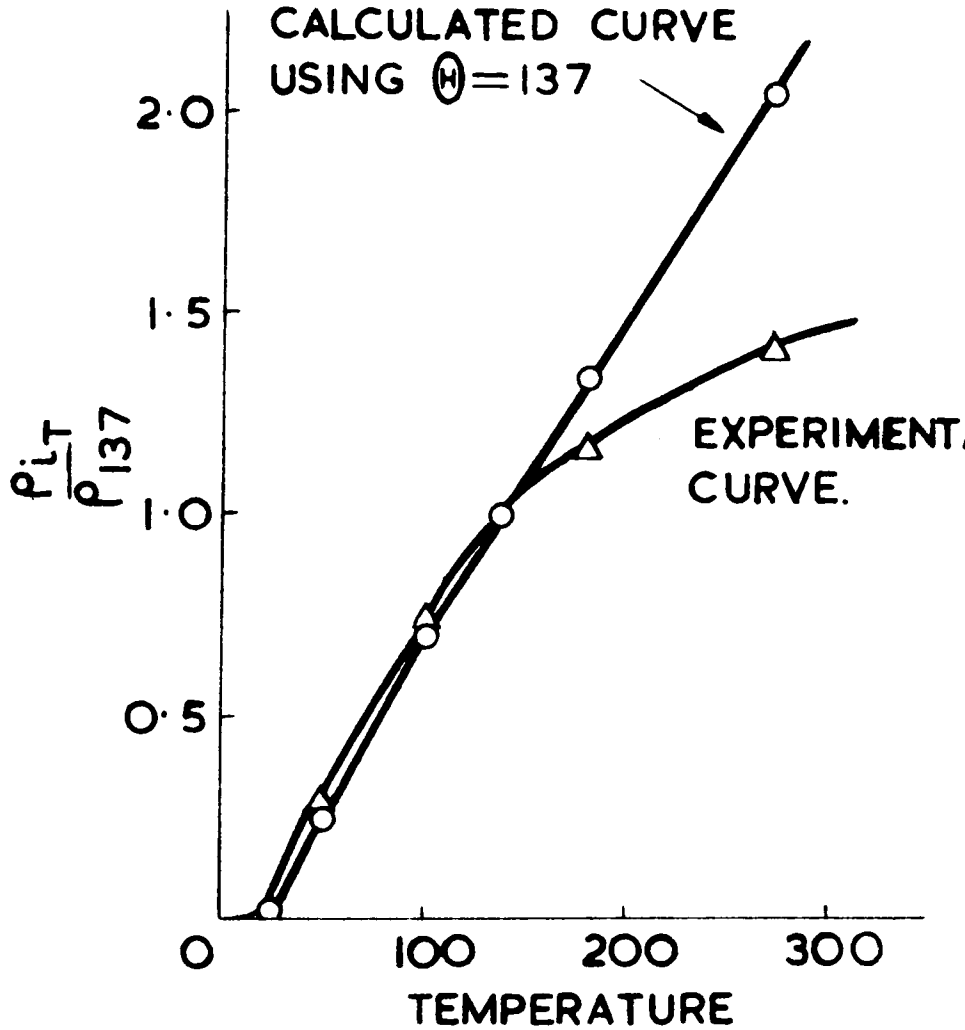


FIG. 3·15

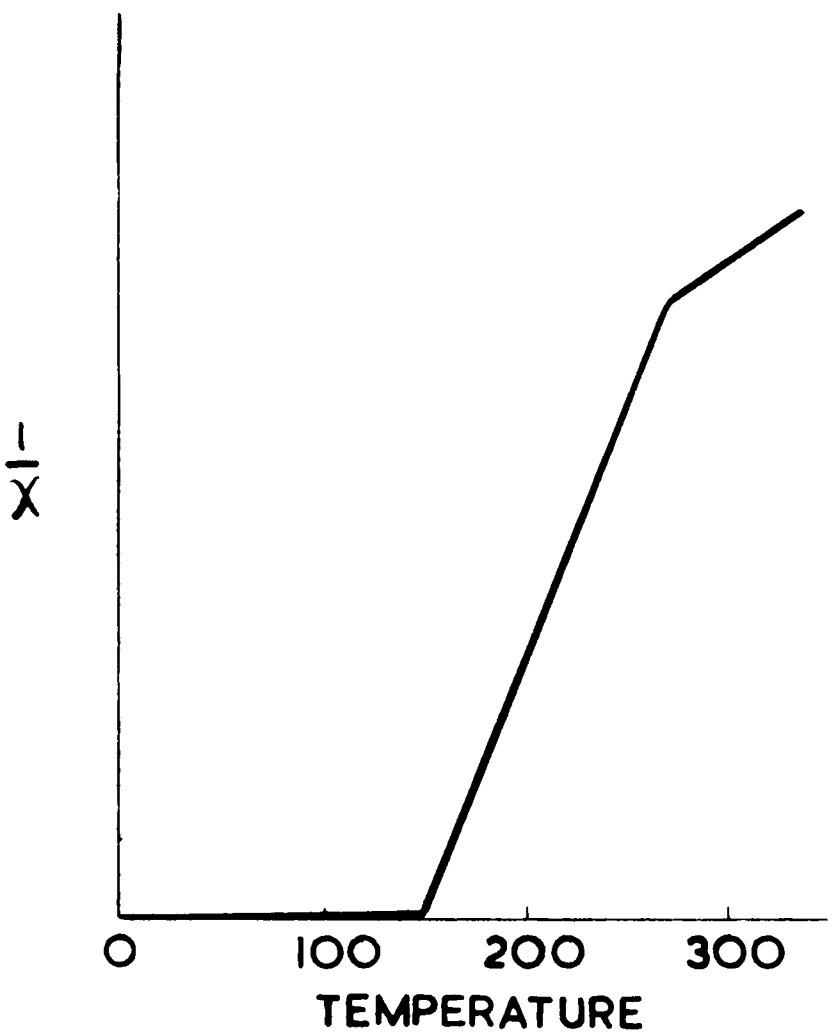


FIG. 3·16

The only other means at the present time of calculating a Θ value for Np is from Lindemann's melting point equation. Determinations from Einstein's formula and the elastic constants are not possible, since there is no compressibility data. The melting point formula leads to Θ_M = 137°K which is comparable with the low temperature Θ_{RS} above. Since the Θ_{RS} of Th and U are lower than the Θ_{DS}, this might possibly be true of Np also.

3.3.2. As mentioned above, the electrical resistivity of Np 1 had previously been measured from room temperature to almost the melting point (Lee, Evans, Hall and King, 1959). In addition, however, E. King (unpubl). had done several runs on this same sample down to 90°K, and had found two small anomalies at about 155 and 273°K. Despite their smallness, their existence was established beyond doubt.

The results of two such runs in the 155°K region are shown in figs. 3.17(a) and (b). The maximum deviation in the anomaly is equivalent to a resistance change of 1 part in 500 in fig. 3.17(a) and 1 part in 2000 in fig. 3.17(b), while scatter of the data appears to be far less than this, perhaps 1 in 10^4. Furthermore, J.D. Hill (priv. comm.), during the course of thermal analysis runs on this material, found small arrests in roughly the same

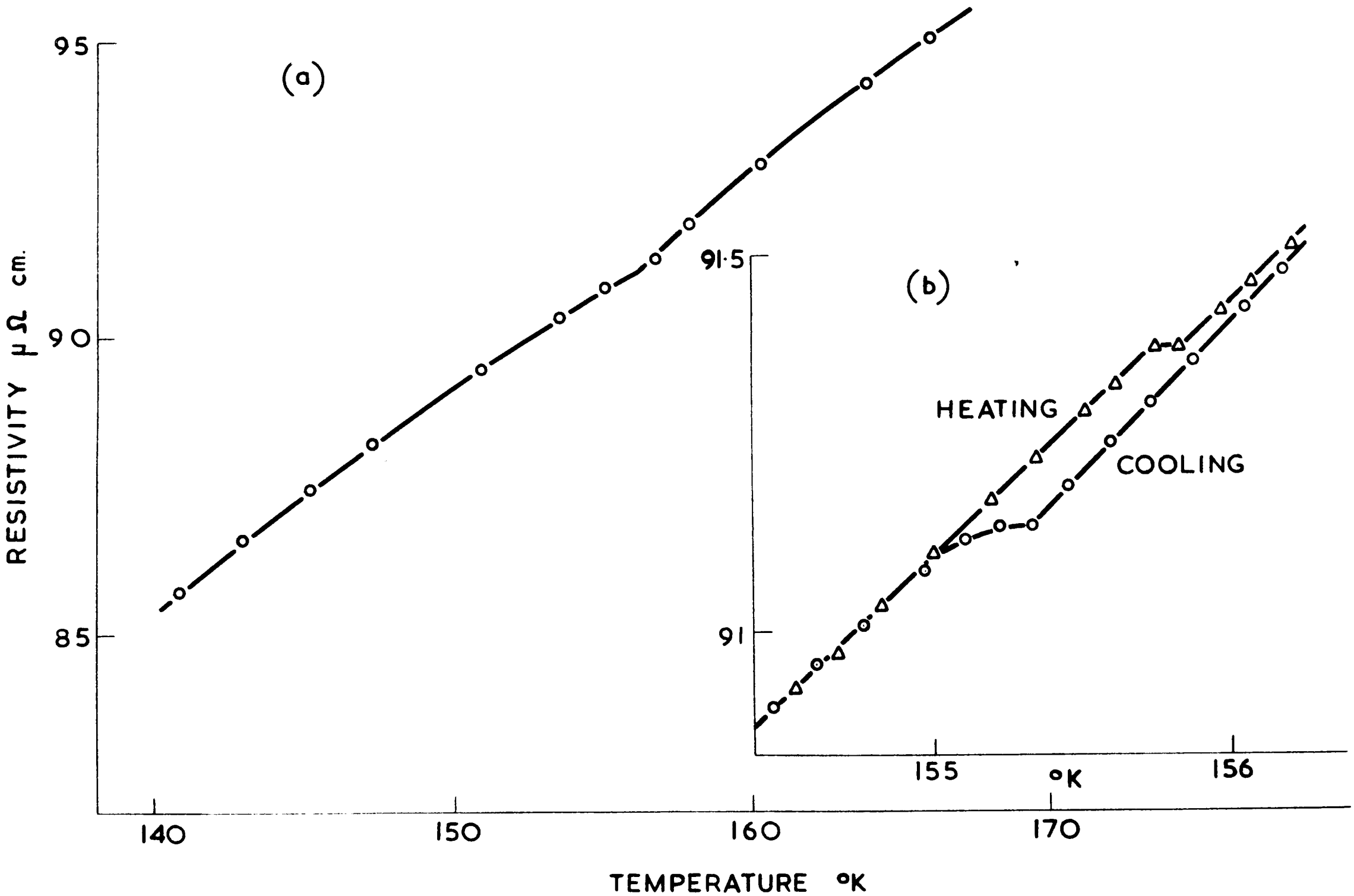
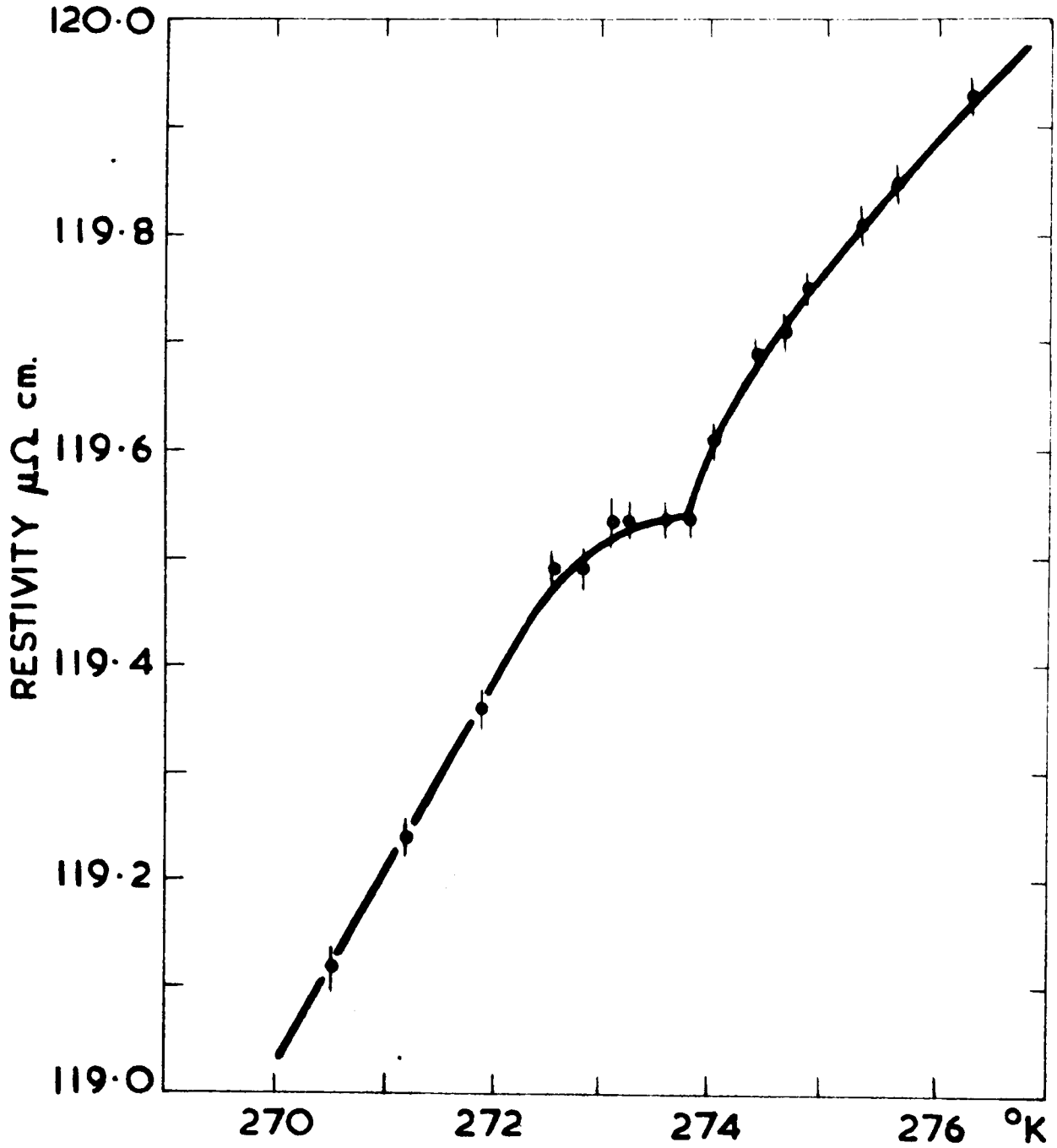


FIG. 3·17 RESISTIVITY ANOMALY AT 155 °K IN Np.

temperature re ions. W.E. Gardner (priv. comm.) then did magnetic susceptibility runs on some of this material, finding two large changes in slope $d\chi/dT$ at these temperatures (see fig. 3.16), the lower one being probably a ferromagnetic transition. He observed no hysteresis at either point. Moreover, annealing the specimen in vacuo to remove any possible hydride made no difference to either the resistivity or the susceptibility. We therefore decided to investigate this problem by making further resistance measurements, but this time on another Np specimen (Np 2) that was to be prepared in a different manner. Firstly, though, a few runs in the region of 155 and 273°K on the original specimen (Np 1) were undertaken.

The anomaly of the type found by King at 155°K was not in fact observed (four runs were done); but there did appear to be some hysteresis, spread over ~5° (153-158°K), equivalent to a resistance change of about 1 part in 2000, on cycling in the region 146 to 162°K (random scatter was about 1 part in 5000).

An example of the 273°K anomaly is given in fig. 3.18. This is typical of the kinks found on our three warming runs and one cooling run. Its magnitude was very small, amounting to 0.05 microhm-cm (in 119) at most, and with a random error of ±0.02 microhm-cm on each point.



THE 273°K ANOMALY IN Np1

FIG. 3.18

The nature of these anomalies is not what one usually expects of magnetic transitions, and neither are they characteristic of crystallographic phase changes. An X-ray diffractometer was used on Np 1 in the region of 273°K, but no noticeable change in the crystal structure was seen. It was thus felt, at this stage, that the anomalies in resistivity and susceptibility, rather than being intrinsic properties of pure Np itself, were most likely due to the presence of a magnetic impurity.

It will be recalled that the Np had a very low purity initially (~99%) and nickel did figure rather high in the analysis report. In fact, the 0.06% Ni would be equivalent to about 1/4% . This alone would probably have been insufficient to have given the observed effects, because Bates and Mallard (1950) have shown that relatively large amounts of iron and nickel can be present in uranium in such a form (e.g. U_6Fe) that the susceptibility is little affected. If this were the cause of the ferromagnetism in Np 1, however, the second specimen, Np 2, would have been affected in the same way, and little could have been learnt by doing further experiments on Np 2. But it was also thought possible that Np 1 could have acquired some additional ferromagnetic impurity during its preparation - perhaps during the arc-

melting or the casting. To settle this last question at least, another specimen was prepared (Np 2) from the same original slug, only this time casting was avoided. It was simply arc-melted into an elongated globule, 14 mm. in length and roughly 4 mm. in diameter. Because of the shortness of the specimen and its thickness, its actual resistance was very low (only 400 $\mu\Omega$ at 295°K). So, in order to regain the sensitivity of the previous measurements, the measuring current had to be raised to the maximum safe limit for the constantan leads in the cryostat viz. 150 ma, and a still more sensitive galvanometer employed.

Let us say at once that no resistive anomalies of any kind were observed in this sample - the slight variations that appeared from time to time being solely the result of random error and possibly varying experimental conditions. Also, no hysteresis or time effects, which could be indicative of the existence of a low temperature crystalline transformation were found whatsoever. Eleven complete runs were done in all. Thermal cycling through the important temperature ranges was coupled with different holding times at low temperatures and different rates of warming. For example, holding time at 77°K or lower was varied from a few minutes to 47 hours, and

warming rates from 77°K to room temperature varied between 1/2 hour and 6 hours.

Moreover, W.E. Gardner (priv.comm.) did not find any magnetic effects in this neptunium specimen, the sample exhibiting ordinary paramagnetic behaviour. Also, G.E. Bacon (priv.comm.) performed a neutron diffraction experiment on this same material at 77°K, and found no evidence for either ferromagnetic or antiferromagnetic behaviour.

Thus, we are led to conclude that Np 1 contained a ferromagnetic impurity of some kind that Np 2 did not have, and that this was the cause of all the various observed anomalies. It is not impossible that this suggested impurity pick-up could have occurred during the arc-melting, as a result of the hearth being contaminated*.

Unfortunately, further spectrographic or chemical analysis on the neptunium was not possible, owing to the relatively high loss of material when doing this. We feel that Np 2 was probably representative of purer metal than Np 1; but any further study must await a future supply of much purer neptunium than is at present available.

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*Indeed, some months later a high purity Pu specimen acquired sufficient impurity during arc-melting for the δ-phase to become stabilised down to room temperature.

3.4. Plutonium.

TABLE 11.

	Density	Length mm	Diam mm	
Pu 1	n.d.	45	2.159	N.P. Cast in silica tube
Pu 2	~19.5	40	1.079	Better purity than Pu 1. Cast in silica tube.
Pu 3	19.625±0.02	30	2.050	H.P. Machined to rod of circular + section.
Pu 3a	19.54±0.12	$19\frac{1}{2}$	~1.29 (D irregular.)	Above spec., remachined.
Pu 4	19.195±0.02	37	2.464	Better purity than Pu 1 or Pu 2. Cast.
Pu 5	18.30±0.04	37	~2.0	Cast specimen from same billet as Pu 3.

The above table gives details of the specimens on which the various electrical resistance experiments were done. Pu 5 in addition was used in the thermopower experiments.

The spectrographic analysis of the billet from which Pu 3 and Pu 5 were obtained is given in the next table (12). This represented the best purity material available at the time. Micrographic examination showed very few

inclusions and certainly no carbide inclusions. Amounts of other actinides, present as impurities, were also likely to be very small. Thus the overall purity was about 99.97 a/o or 99.99 w/o.

Analyses for Pu 2 and Pu 4 are also included in table 12.

The densities of most of the specimens were very high, and compared well with the value from X-ray studies of 19.82 gm/cc. In even high purity Pu, the density is generally only 19.3 to 19.6 gm. per cc., especially of cast material. This is because Pu has as many as six allotropes between room temperature and the low melting point of 640°C. The lower temperature phases have complex crystal structures, and large volume changes are associated with transitions between them. Consequently, thermal cycling (or merely cooling after, for instance, casting or annealing) sets up internal strains, and leads to the formation of microvoids and the retention of lower density, higher temperature phases. This often has marked effects on experimental measurements conducted above room temperature, and accounts in part for the differing values hitherto reported by various workers for the common physical properties.

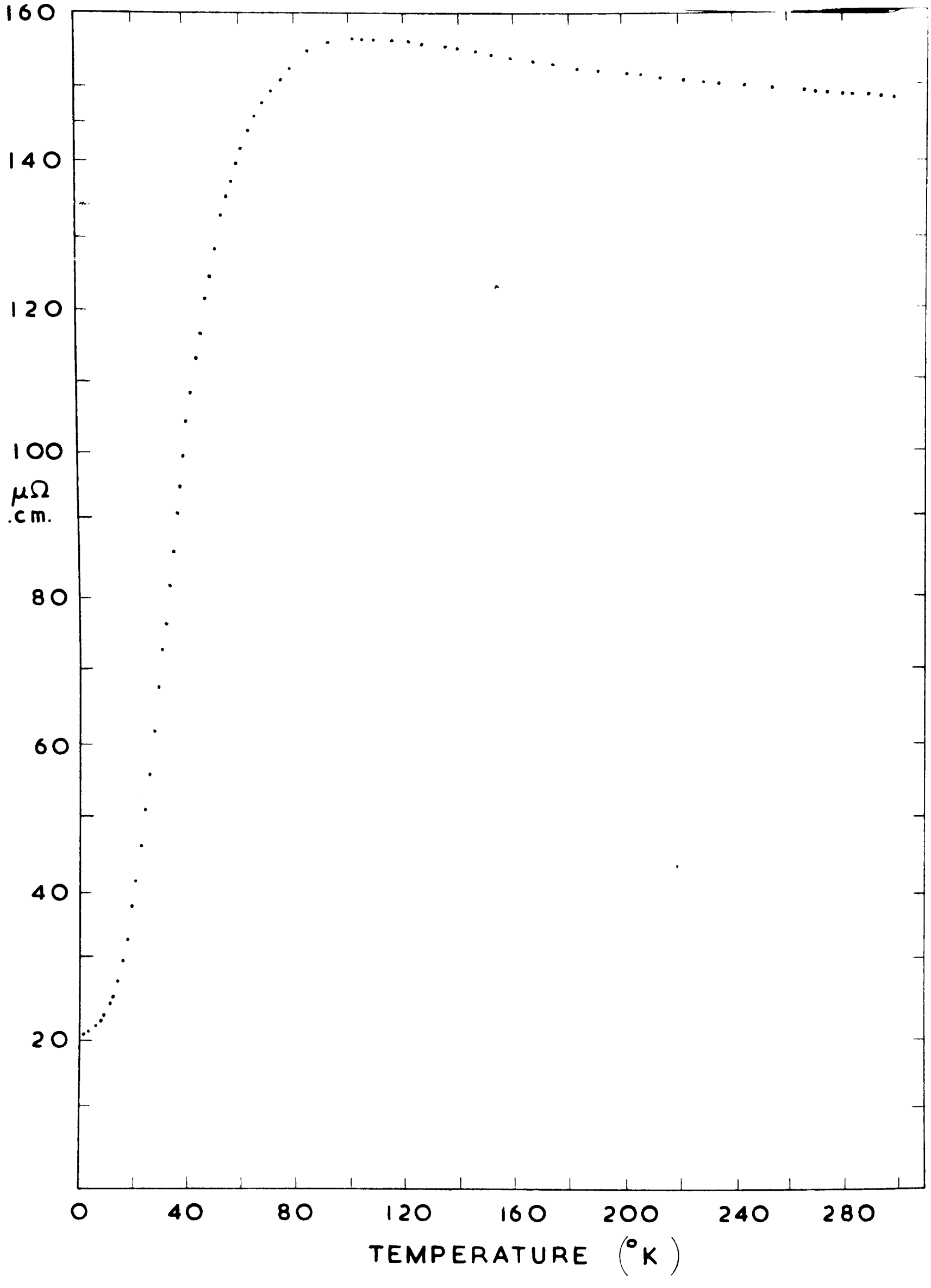


FIG. 3·19. ELECTRICAL RESISTIVITY OF Pu 3 (RUN 5.)

TABLE 12.

Spec. Analysis of Billet from which Pu 3 and Pu 5 were obtained.

Cu	Mg	Mn	Ni	Pb	Si	Sn	Cr	Fe
5	80	10	17	19	~20	8	1	40 ppm.

Not detected:

Al	Ag	As	Au	B	Be	Bi	Cd	Co
< 2	1	20	1	1	0.6	1	15	10

Ge	In	Mo	P	Pd	Sb	Ti	Tl	V	W	Zn
1	2	7	80	<20	20	400	1	10	200	60

Spec. Analyses of Billets from which Pu 2 and Pu 4 were obtained

	Fe	Ni	Cr	Si	Ca	U	Th
Pu 2	70	60	20	<25	30	<50	
Pu 4	45	15	<5	<25	65	<50	100

No isotopic analysis on our samples was carried out, but, judging by published values by other workers, it would have been roughly ~ 95 % Pu^{239}, $4\frac{1}{2}$ % Pu^{240}, 1/4 % Pu^{241} and 0.05 % Pu^{242}. The mean atomic weight is thus roughly 239.1 on the physical scale. The half-life of Pu^{239} with respect to α-disintegration is 24,110 years and the associated self-heating 1.92 milliwatts per gm. (Stout and Jones, 1947). In point of fact, Pu^{240} significantly contributes to the self-heating as well, so that for our specimens it was nearer 2.2 milliwatts per gm.

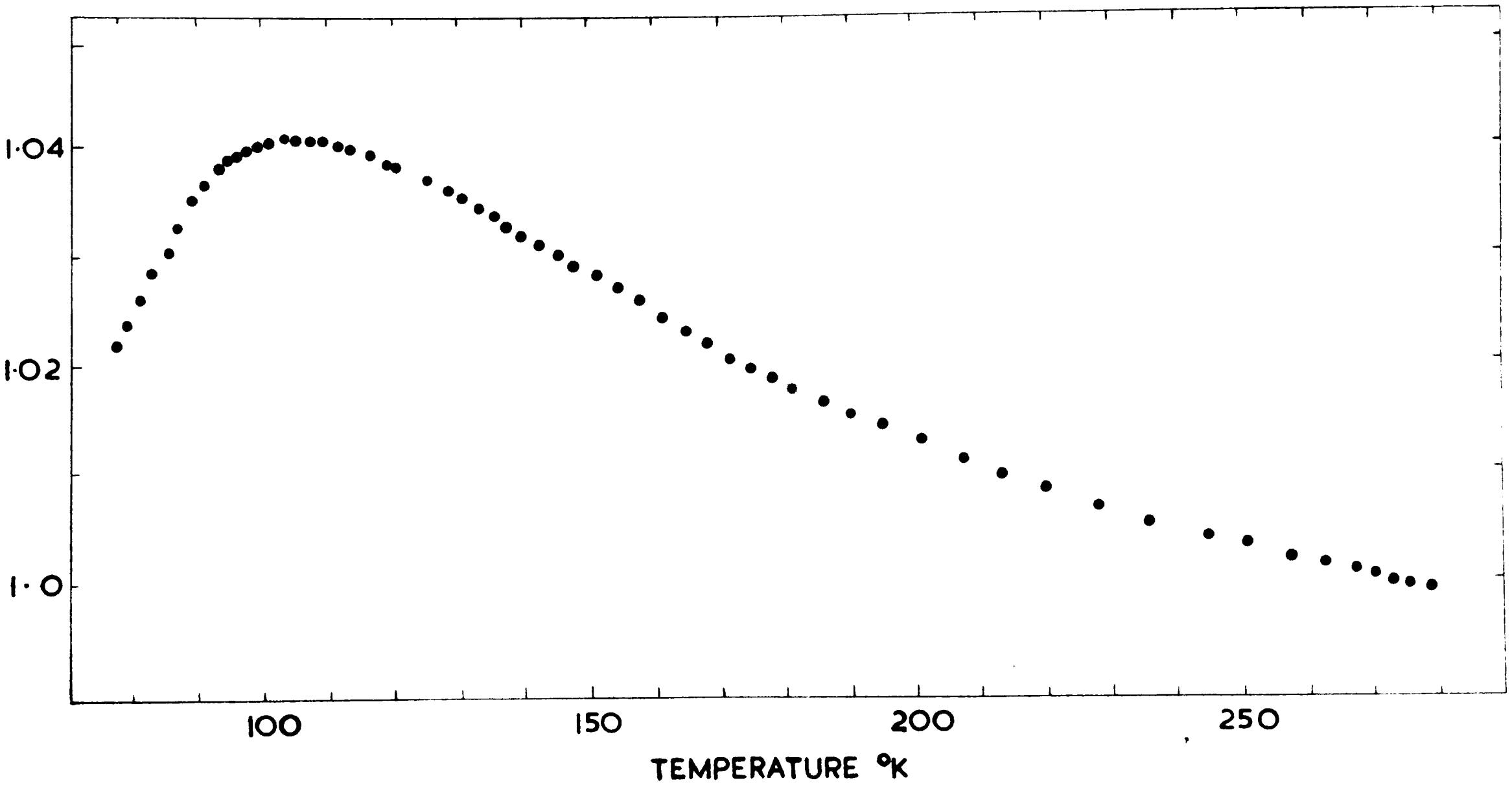


FIG.3-20 RESISTANCE OF Pu 3 — RUN 3 (WARMING)

3.4.1. The first experiments on Pu 1, Pu 2 and Pu 3 were carried out with them canned in the manner described in section 2.2. This work was commenced before the "active" cryostat had reached completion.

Pu 1 gave a lot of trouble because of faulty spot-welded contacts, and dynamic measurements on it were out of the question. It was ascertained, however, that its residual resistance was very high (25-30% of the room temperature value), and also that it was not superconducting at a temperature of 1.40°K. The other canned specimens (Pu 2 and 3) were taken to the Clarendon Laboratory and, like Np 1 and U1, were cooled to 0.75°K. Neither sample was found to be superconducting at this temperature. For Pu 2, the residual resistance ratio* was 0.26, while even for the high purity Pu 3 it was 0.14 (contrast with the low ρ_o, and yet the low purity of Np 1). The significance of these high values will be discussed later in Chapter 5 (section 5.5.4.).

The results of one of the earlier warming runs from 1.4°K to room temperature on Pu 3 are shown in fig. 3.19 (see also fig. 3.20). The anomalous behaviour of the

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* By this term we mean the ratio of the residual resistance (usually at 4°K) to that at room temperature. i.e. $\rho_{4.2}/\rho_{295}$

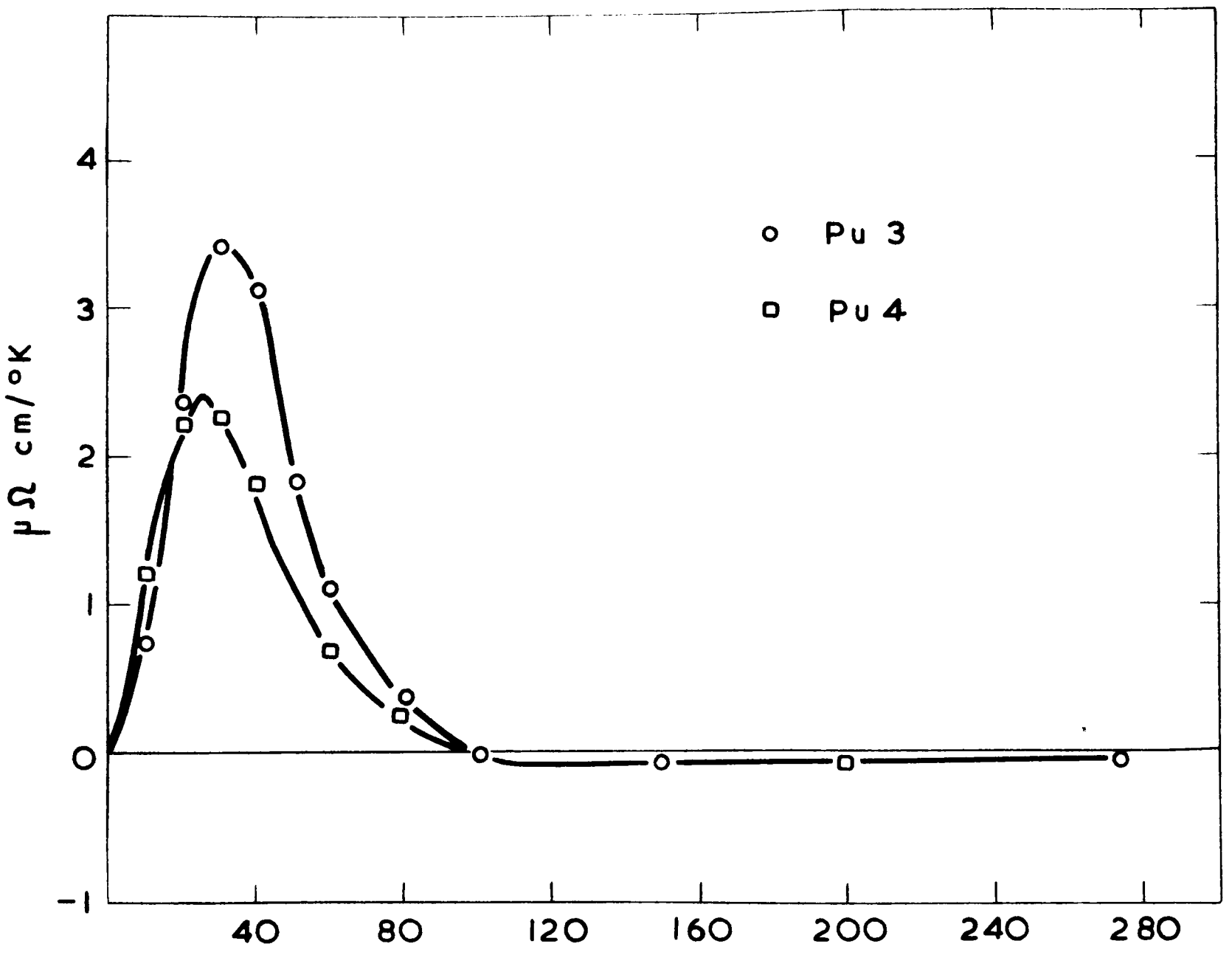


FIG. 3·21

resistance as a function of temperature is quite remarkable, and one is immediately reminded of α-manganese in this respect. Besides the high residual resistance, two features are of exceptional interest, viz. the very high positive temperature coefficient between 20 and 60°K, and the low negative temperature coefficient above 105°K (fig. 3.2 1.). This slowly falling resistivity continues beyond room temperature, in fact all the way to the α-β phase change at 390°K. The temperature coefficient is, moreover, negative in the β- and γ- phases as well (see, for example, Sandenaw and Gibney (1958), or fig. 5.3 due to King).

The behaviour of Pu 4 was entirely similar. This specimen was slightly less pure than Pu 3, and, in addition, had been cast into shape rather than machined. Pu 3, on the other hand, had been machined in order to ensure that its original high purity was maintained. The data of run 1 on Pu 4 is compared with Pu 3 in Table 13. It will be seen at once that ρ_o is higher than ever (32% of the room temperature reading), yet the room temperature resistivities of both specimens differ but little. ρ_{max} is a little less accentuated in Pu 4, but occurs at the same temperature (105°K). In neither specimen had the resistance become constant at 4.2°K, but it continued to fall to 2°K at least.

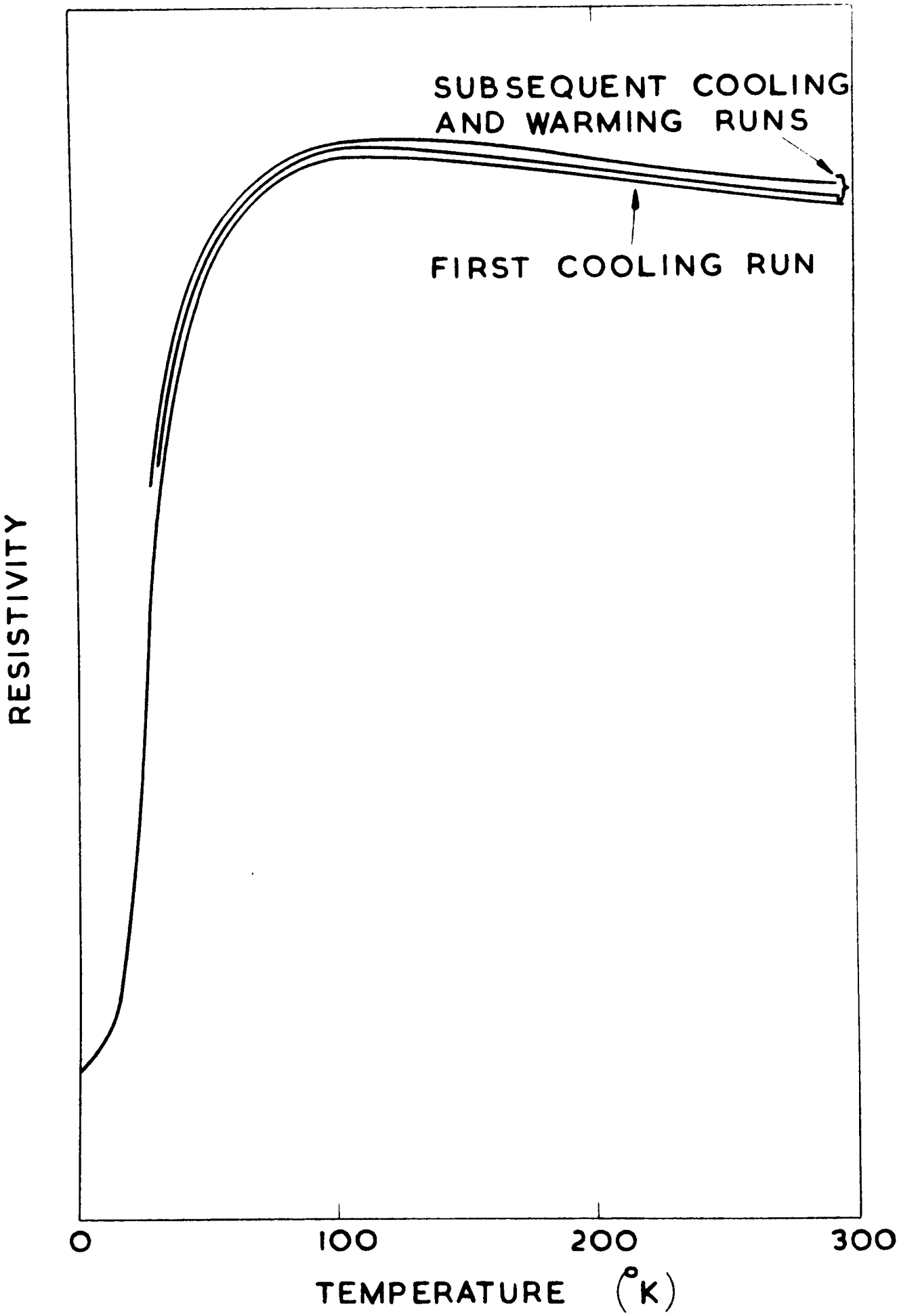


FIG. 3·22. HYSTERESIS EFFECTS IN PLUTONIUM.

We should add that the isotropy of these specimens had been found to be very good.

3.4.2. Another thing that was frequently found with either specimen was that the room temperature resistivity increased in value as the result of a low temperature run, but that it partially returned to its initial value during the next few days. The magnitude of this increase was never very great ($\gtrsim$ 1-2%), and it could be quite reasonable and sufficient to suppose that it arose simply as a result of the thermal cycling within the very anisotropic α-phase, and that the subsequent decrease was due to room temperature annealing.

On the other hand, it was not impossible that there might exist yet another crystallographic modification of Pu, stable only below some definite temperature below room temperature. Low temperature phase changes are very often sluggish, and frequently partial retention of the low temperature modification occurs, even when the metal has warmed considerably above its "normal" transformation temperature. Any such retention would be very likely in Pu, where microdamage between highly anisotropic phases could be considerable (as with the α-β, β-γ phase changes). Differences between cooling and subsequent warming curves

TABLE 13.

	Pu 3		Pu 4	
	ρ_T	$d\rho/dT$	ρ_T	$d\rho/dT$
	$\mu\Omega cm$		$\mu\Omega cm$	
1.4°K	20.75	0	49.25	0
10	22.6	+0.75	55.1	+1.21
20	39.3	2.36	72.4	2.21
40	102.6	3.12	117.8	1.81
60	140.1	1.10	142.0	0.72
80	152.5	0.37	152.0	0.28
100	155.5	+0.005	155.6	+0.005
150	153.6	-0.061	154.8	-0.040
200	150.9	-0.041	153.0	-0.034
250	148.9	-0.031	151.4	-0.031
273	148.1	-0.026	150.8	-0.026
300	147.5±0.2	-	150.5±0.2	-

would then arise on account of the differences in composition of the sample at each temperature, so that it would be possible to study the transformation by a series of suitable thermal cycling experiments.

Now Sandenaw and Olsen (1960) in their Grenoble Conference report said that they had obtained hysteresis

effects between 48°K and room temperature as a result of continued thermal cycling between 48 and 63°K, combined with holding at 48°K and employing various warming speeds back to room temperature. They attributed this to a transformation to another (unnamed) state that took place between 48 and 63°K, and linked it with a specific heat peak at 50°K (Sandenaw, Olsen and Gibney (1960), see fig. 5.5). Our work, however, most of which was done before the Grenoble Conference, but a little of which was necessarily done after the publication of Sandenaw and Olsen's paper, went further than this.

While confirming that the above observations of Sandenaw and Olsen were correct, we found that it was immaterial whether the cycling run was done between room temperature and 4°, 20°, 50° 77° or even (to a lesser extent) 130°K. Each time, the warming curve was higher than the cooling path before. A certain amount of recovery took place on holding at room temperature, though never sufficiently for the first cooling curve of all ever to be followed again. This suggested that a certain amount of damage had occurred that did not (or could not) anneal out at room temperature.

Furthermore, there did not appear to be any additional effect as a result of prolonged holding for 8 hours at

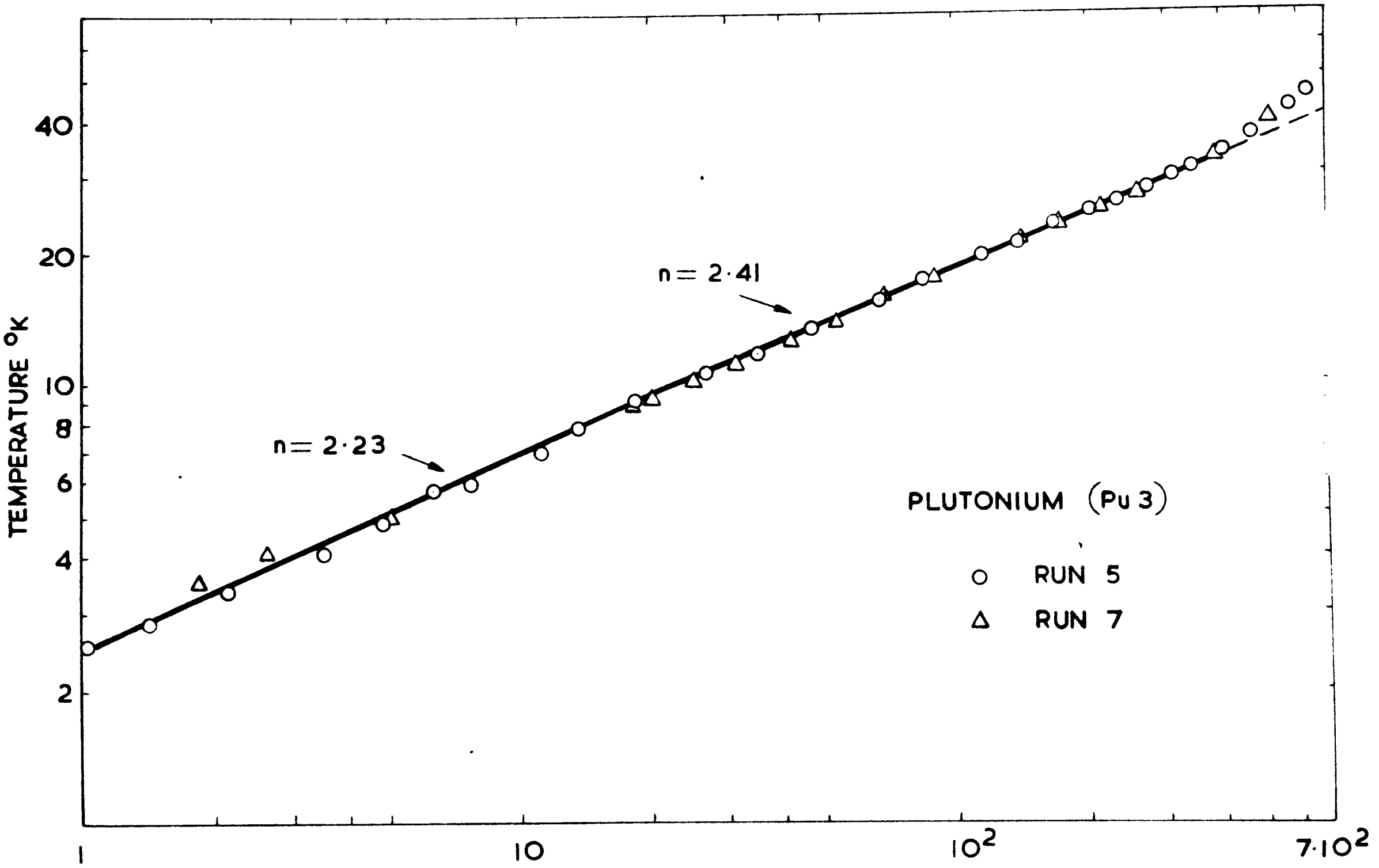

TEMPERATURE °K
40
20
10
8
6
4
2
n = 2·41
n = 2·23
PLUTONIUM (Pu 3)
RUN 5
RUN 7
1
10
10²
7·10²
'IDEAL' RESISTANCE (ARBITRARY UNITS.)

FIG.3·23

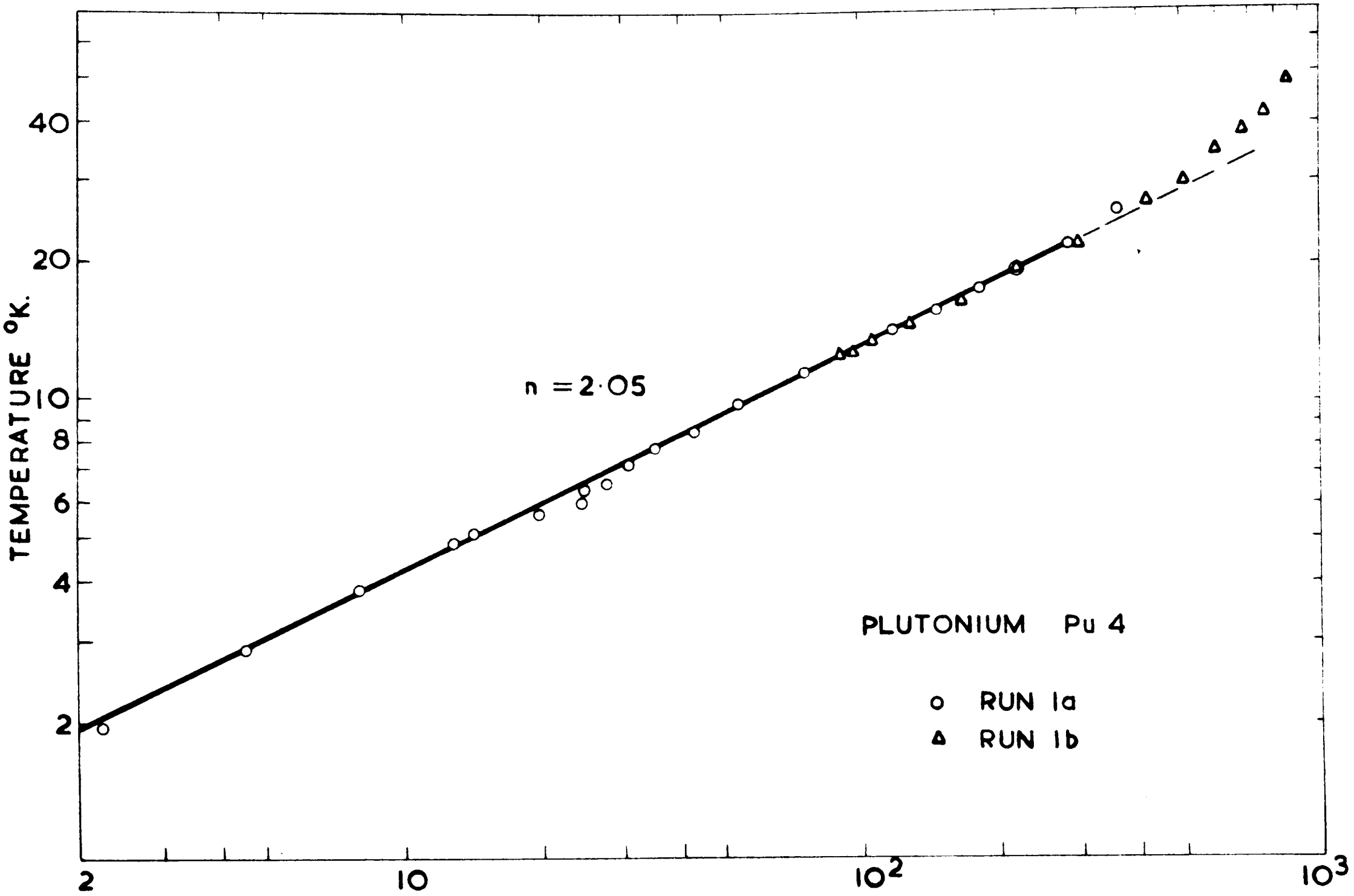


FIG. 3·24 IDEAL RESISTANCE (ARBITRARY UNITS)

4.2°K, or for 20 hours at 77°K. Also, any change in resistivity did not appear to be significantly different, whether the thermal cycling was done between 50 and 77°K, or between 20 and 77, or between 4 and 50°K. Lastly, as a result of the series of runs on Pu 3, it was found that both the room temperature resistivity and the residual resistivity showed a net increase of about the same amount (1%).

We are thus led to conclude that the observed hysteresis effects are simply the result of cold work occurring in the metal during thermal cycling, and that there is no evidence at all for a transition temperature between 48 and 63°K (as suggested by Sandenaw and Olsen) or at any other temperature below 100°K. Certainly, if any low temperature phase does exist, its effect on the resistivity above the transformation temperature is very small, and is almost if not wholly masked by the unavoidable cold work taking place on thermal cycling in the α-phase.

3.4.3. The various sequences of runs to study the hysteresis effects mentioned above were carried out on specimens Pu 3, Pu 4 and Pu 3a. The latter specimen had originally been prepared from Pu 3 (diam. 2 mm.) by

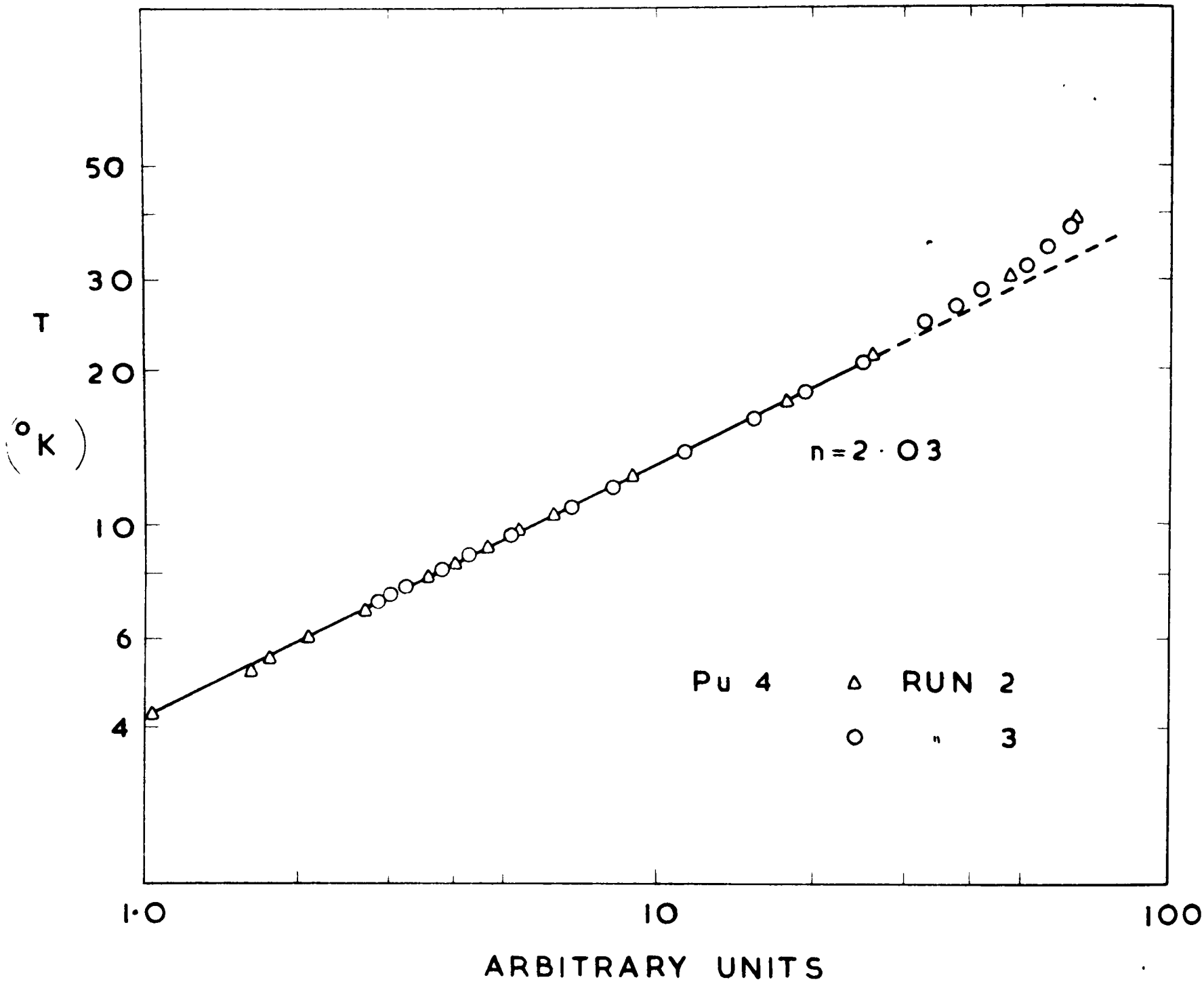
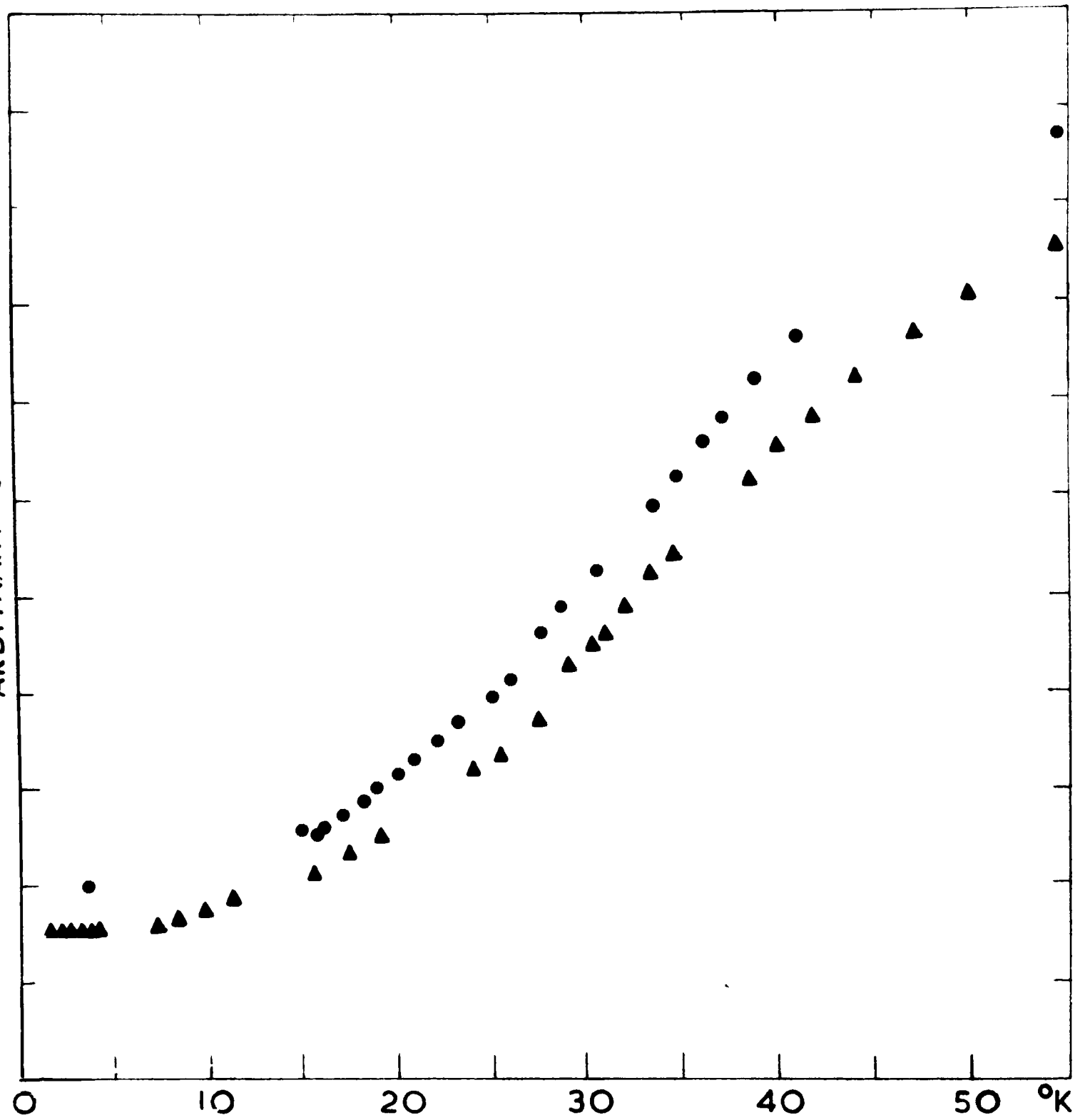


FIG. 3·25. IDEAL RESISTANCE vs. TEMP.

additional machining, in order to see whether the sample dimensions by way of the high self-heating had any significant effect on the resistive properties. The lathe-work involved proved very difficult, Pu being rather brittle and the work having to be done in a glove-box, with the result that we had to be content with a specimen of irregular diameter 1.29 mm. and length 20 mm. However, we found no significant change in either the residual resistivity or in the shape of the ρ -T curve.

Logarithmic plots of R_i vs. T for the low temperature data are given in figs. 3.23 and 3.24. It will be seen that in Pu 4 the resistance obtained after subtracting the residual resistance is almost exactly proportional to T^2. Because of the fair scatter, two more runs were done, and graphs for these are shown in fig. 3.25. In the rather purer specimen Pu 3, the index of T was a little higher, being 2.4 between 8 and 27°K, though it is nearer 2.2 below 8°K. The ideal lattice resistance at these temperatures appears to be entirely swamped by the mechanism causing the sharp rise and peak in the R-T curve.

3.4.4. Sandenaw and Olsen (1960) also reported the existence of a resistive anomaly at 27°K on one specimen and 31° on another, and we reproduce their curves in fig.



ELECTRICAL RESISTIVITY CURVES FOR Pu.
(SANDENAW AND OLSEN, 1960)

TWO RUNS ON THE SAME SPECIMEN.
ORDINATES HAVE BEEN DISPLACED TO SEPARATE THE CURVES.

FIG. 3.26

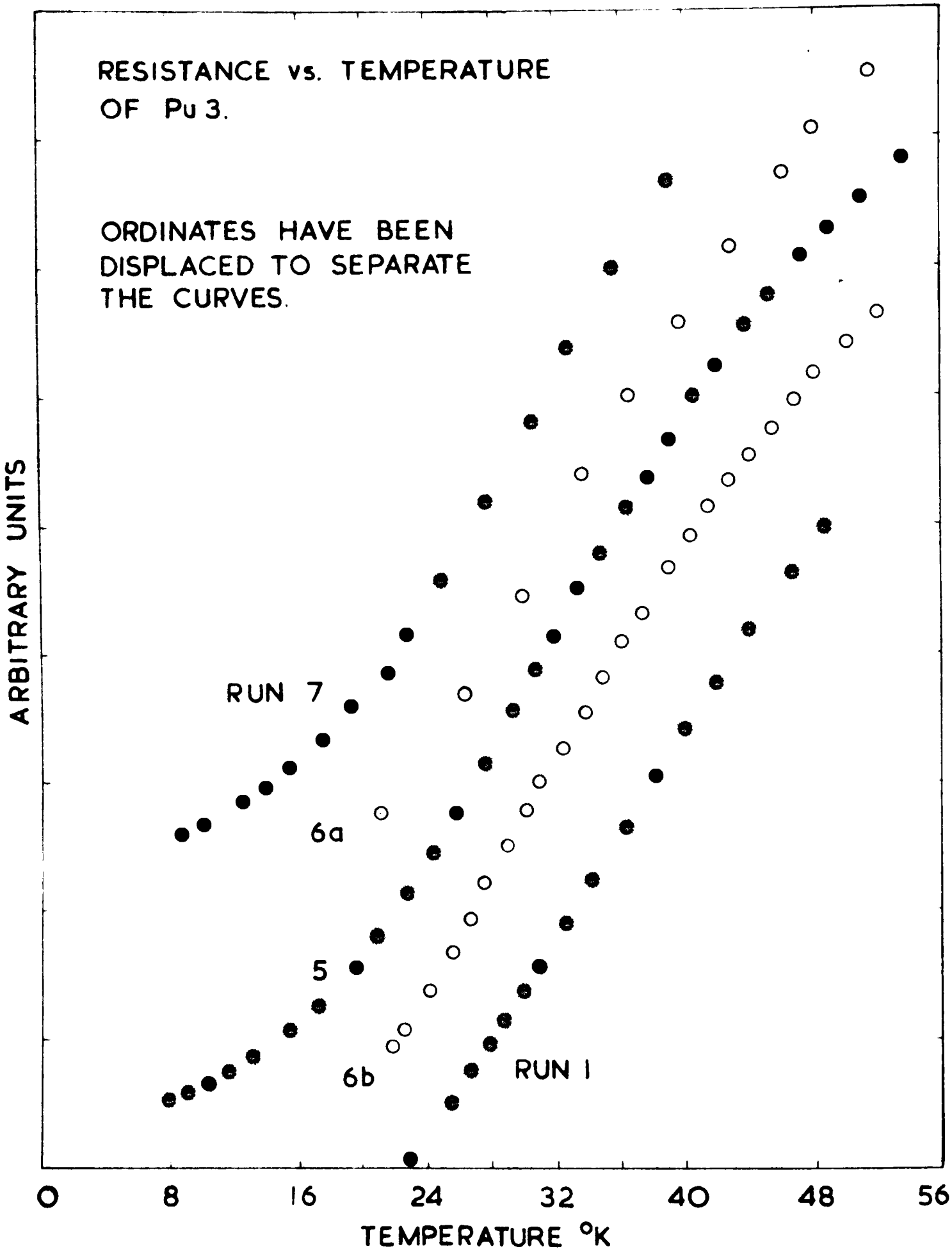
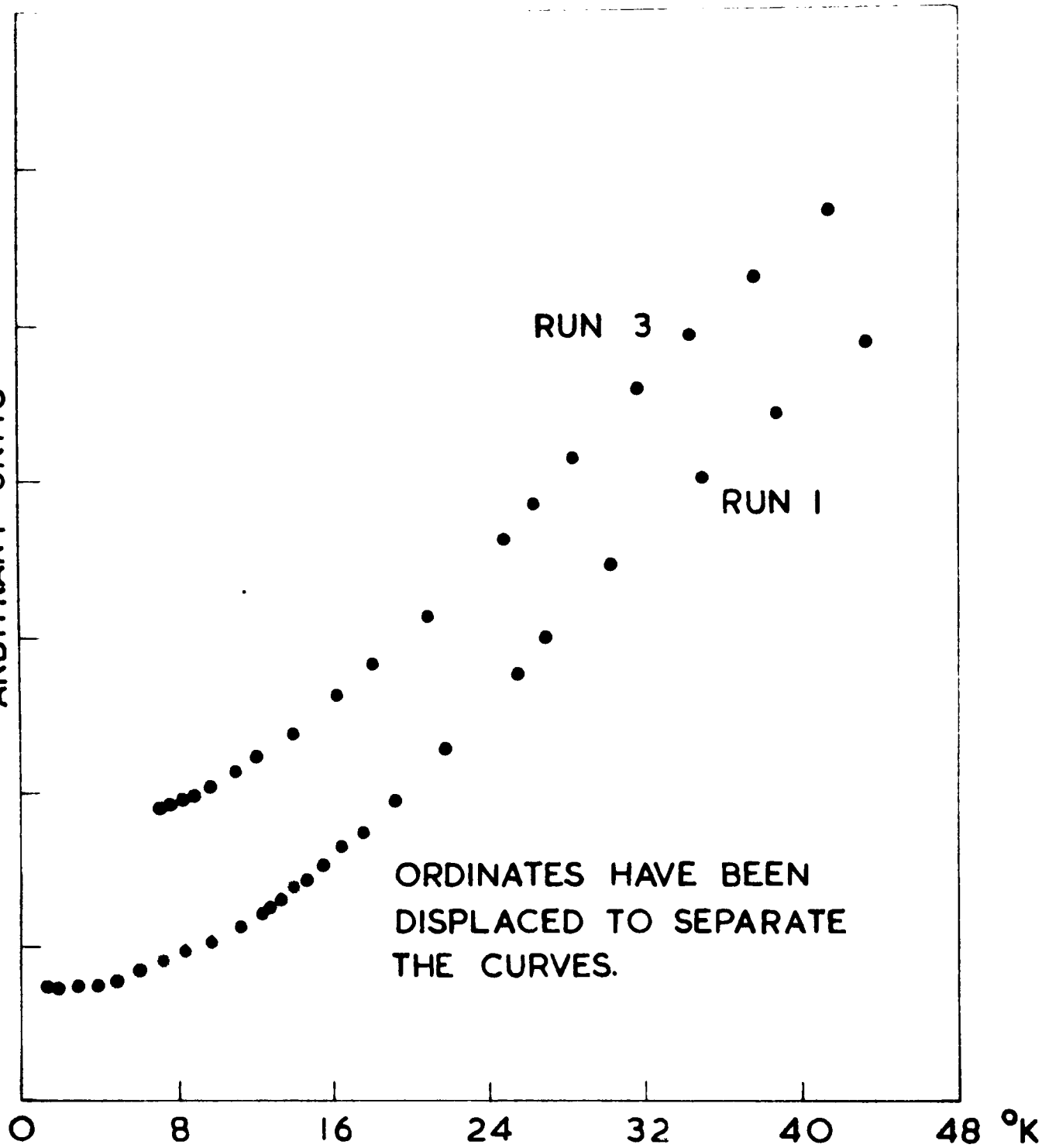

RESISTANCE vs. TEMPERATURE
OF Pu 3.
ORDINATES HAVE BEEN
DISPLACED TO SEPARATE
THE CURVES.
ARBITRARY UNITS
RUN 7
6a
5
6b
RUN 1
0
8
16
24
32
40
48
56
TEMPERATURE °K

FIG. 3.27



RESISTANCE vs. TEMPERATURE OF Pu 4.

FIG. 3.28

3.26. A peak in the specific heat at about this temperature had already been found by the same workers (Sandenaw, Olsen and Gibney (1960), see fig. 5.5). We thereupon re-examined our curves in this temperature region, and these are shown in figs. 3.27 and 3.28. As can be seen, there does not appear to be any kind of anomaly on our graphs, even though there is less scatter on our data than on Sandenaw and Olsen's. Our specimens, however, were purer than theirs, and had a much lower ferromagnetic impurity content. Whereas Sandenaw and Olsen's two specimens had combined Ni and Fe contents of 150 and 400 p.p.m., those of our specimens, Pu 3 and Pu 4, were only 57 and 60 p.p.m. respectively.

3.4.5. It is not possible, of course, to derive characteristic temperatures for Pu from resistance data, but, for purposes of comparison with the preceding actinide metals, we thought it profitable to do so by other means.

From the elastic constants we obtained $\Theta_{El} = 149^{\circ}K$ and from Einstein's formula we found $\Theta_{E} = 127^{\circ}K$, whereas the use of Lindemann's melting point formula gave us an intermediate value $\Theta_{M} = 135^{\circ}K$. These figures compared with 171 to $176^{\circ}K$ calculated from Sandenaw, Olsen and Bibney's specific heat data.

We thus see that all the various ways of calculating characteristic temperatures for the four actinide metals that we are considering lead to values within the range 100 to 200°K. If we limit ourselves to probable values determined from specific heat data, this range is narrowed to 150 to 190°K. If, further, we restrict ourselves to a single value for each metal, the best compromise appears to be Th ~ 160, U ~ 170, Np ≈ 150 and Pu ~ 170°K.

3.5. Metastable δ-Plutonium.

The δ-phase of plutonium, which has a face-centred cubic crystal structure, is stable within the temperature range 320°C to 450°C. This phase can be stabilised to room temperature by alloying with certain other metals, provided that the valency differences and size factors are favourable. Thus, the addition of 2 to 13.5% aluminium will stabilise the δ-phase down to room temperature, though these concentration limits are a little less if stabilisation to helium temperatures is required. The practical importance of such f.c.c. alloys is that they are more easily worked metallurgically than the monoclinic α-phase.

Resistance measurements were made on three samples, details of which are given in table 14. Each specimen was prepared by arc-melting, followed by casting in a precision-

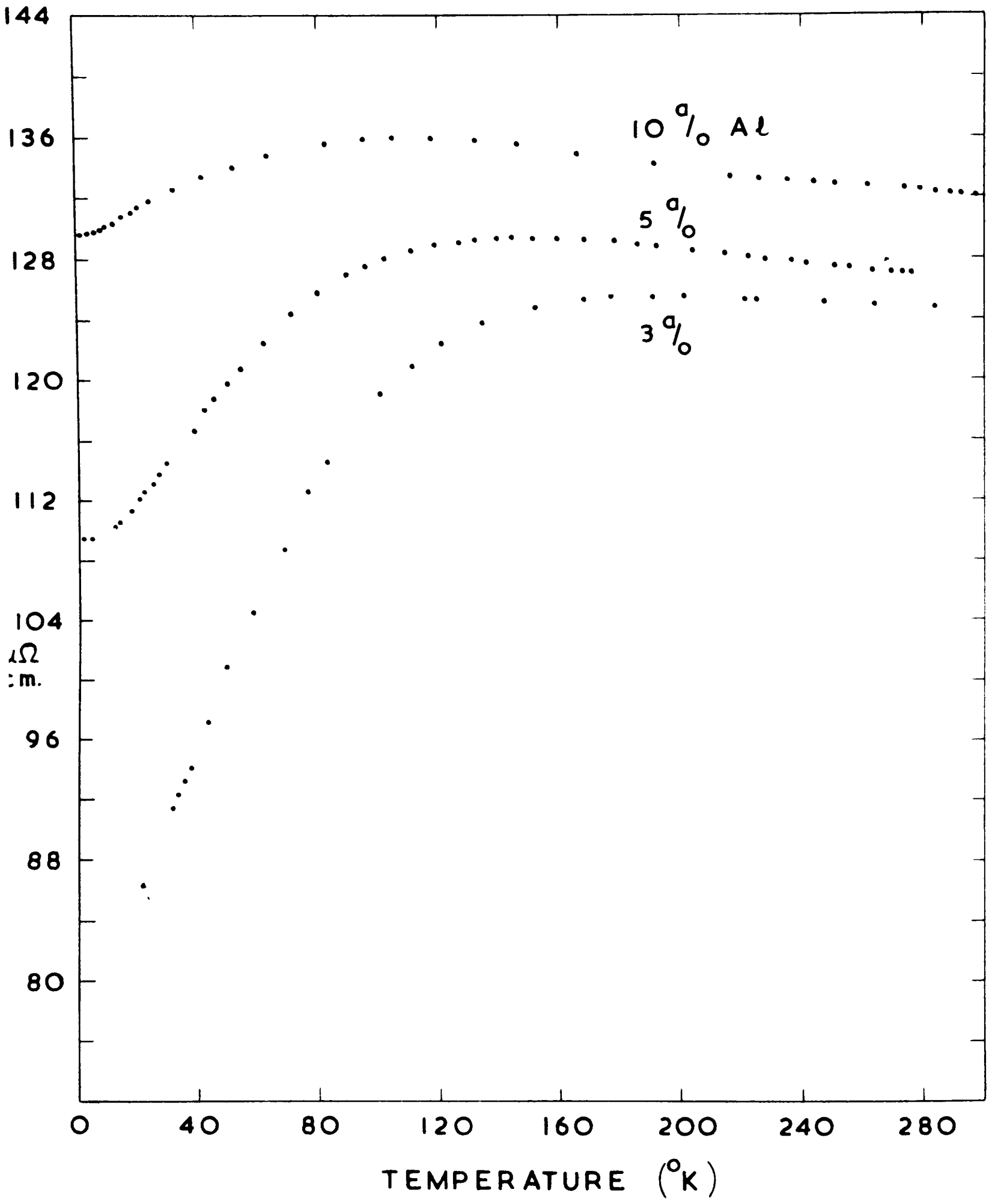


FIG. 3 29. ELECTRICAL RESISTIVITY OF δ – Pu–Aℓ ALLOYS.

TABLE 14.

Specimen	Length mm.	Diameter mm.	As Cast Density gm./cc.	Theoretical Density
3 % Al-Pu	12	2.240	15.56	15.74
5 % Al	32	2.269	15.19	15.51
10 % Al	30	2.207	14.39	15.18

bore silica tube. The best available Pu and Johnson-Matthey spectroscopically-pure Al were used in the preparation of the alloys.

The as-cast densities were lower than the calculated ones, being as much as 5% lower in the case of the richest Al alloy. This could have been because the actual compositions of the alloys were not the same as the intended compositions, or because of the formation of microvoids. However, it was sufficient for the essentially qualitative nature of our work on these alloys to take the actual and intended compositions as being the same.

From the results, which are presented in fig. 3.29, it can be seen that the resistance-temperature relationships bear a close resemblance to that of α-Pu. The resistance rises to a maximum in the region 100 to 200°K, above which the temperature coefficient is small and negative.

Increasing the solute content lowers the temperature coefficient at low temperatures, and moves the maximum itself to lower temperatures. None of the alloys incidentally showed any sign of superconductivity at 1.50°K.

CHAPTER 4.

The Thermoelectric Power of the Actinide Metals from 20 to 300°K

As explained in section 2.9 when describing the procedure involved, the thermoelectric power of each metal in turn was measured relative to the power of the copper of which the copper-constantan thermocouples were composed. The only means of determining the absolute power of this copper was to measure it relative to another metal, which could be accepted as a standard. Such a metal is lead, whose absolute thermoelectric power has recently been determined at low temperatures by Christian, Jan, Pearson and Templeton (1958) at N.R.C., Ottawa (see also Jan, Pearson and Templeton (1955) and Pearson and Templeton, 1955). These authors' measurements on lead were carried out between 7 and 18°K relative to superconducting Nb_3Sn. This left only a small region, 18 to 20°K, across which the Thomson heat of lead had to be interpolated in order to join on to the values of Borelius, Keesom, Johansson and Linde (1931, 1932). A small correction to the latter's values above 20°K was found to be necessary (see Tables 1 and 2 in C.J.P.T's paper).

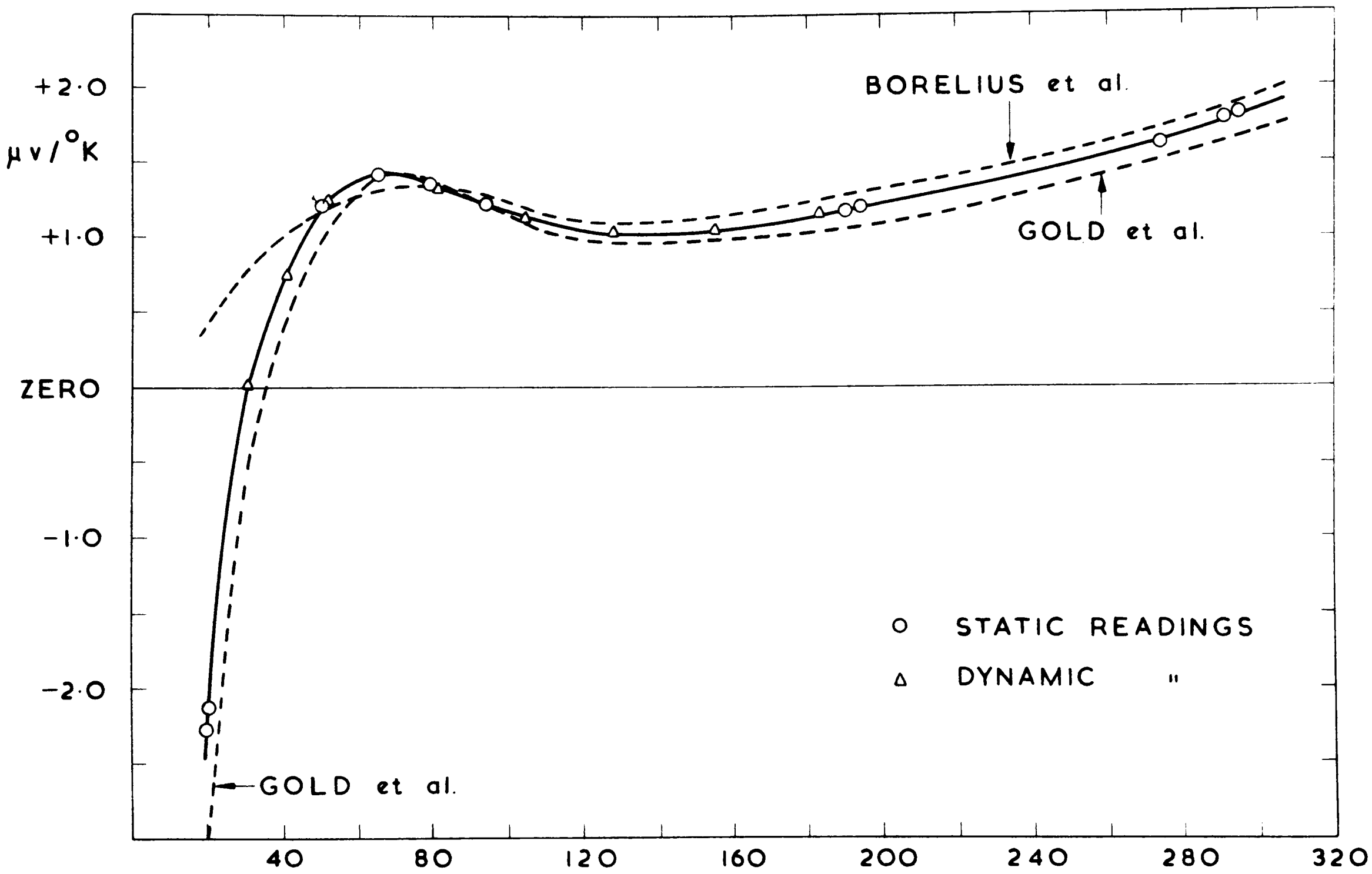


FIG. 4·1. ABSOLUTE THERMOELECTRIC POWER OF COPPER.

4.1. Copper.

Following C.J.P.T., "spectroscopically pure" lead was obtained from Messrs. Johnson, Matthey and Co Ltd., and the specimen formed by vacuum casting into a rod 2 mm. in diameter and $5\frac{1}{2}$ cm. in length. The two thermocouple beads were soldered to the specimen about 3 cm. apart with Wood's metal.

The absolute thermoelectric power of the copper was obtained by adding algebraically the power of lead to the measured thermoelectric power of the lead-copper thermocouple. Our results for copper over the range 20 to 300°K are shown in fig. 4.1. For purposes of comparison, the results of Borelius et al (1930) and Gold, MacDonald, Pearson and Templeton (1960) are also included.

These last-named authors found that several of their specimens displayed a most remarkable decrease in thermoelectric power on cooling to low temperatures, and which culminated in a large minimum at about 9°K. Below 30 to 40°K, in fact, not one of their specimens resembled in behaviour the previously accepted values of Borelius et al. It will be seen at once that below 50°K our curve, like Gold et al's, is also descending to a deep minimum, but that above 50°K agreement between all the curves is quite reasonable.

This minimum has been explained by Cold et al. as being specifically caused by the presence of trace amounts of iron in solid solution. They showed that other impurities were only of minor importance and that the minimum was almost, if not completely, absent if the iron was present as an oxide. Thus it was that some of their purest specimens, with only 1 p.p.m. of iron, showed the greatest anomalies in the thermoelectric power.

Now the oxygen-free, high-conductivity copper used in our thermocouples was supplied to us by the manufacturer expressly for use as thermocouple wire. For this purpose it is quite satisfactory down to 20-25°K, if used against constantan, since the absolute power of constantan is so very large above these temperatures. But, as an absolute standard itself, even though calibrated against lead, it is not very suitable below 30°K or so, because of its large temperature coefficient. It is unfortunate that, so long as there is some iron present (~ 1 ppm), then the purer the copper is, the more anomalous its thermoelectric power at low temperatures is likely to be. Evidently, copper should never be used as a thermoelectric standard at low temperatures unless it has been independently calibrated against a metal, such as lead, whose reliability has been proved. It would perhaps be better

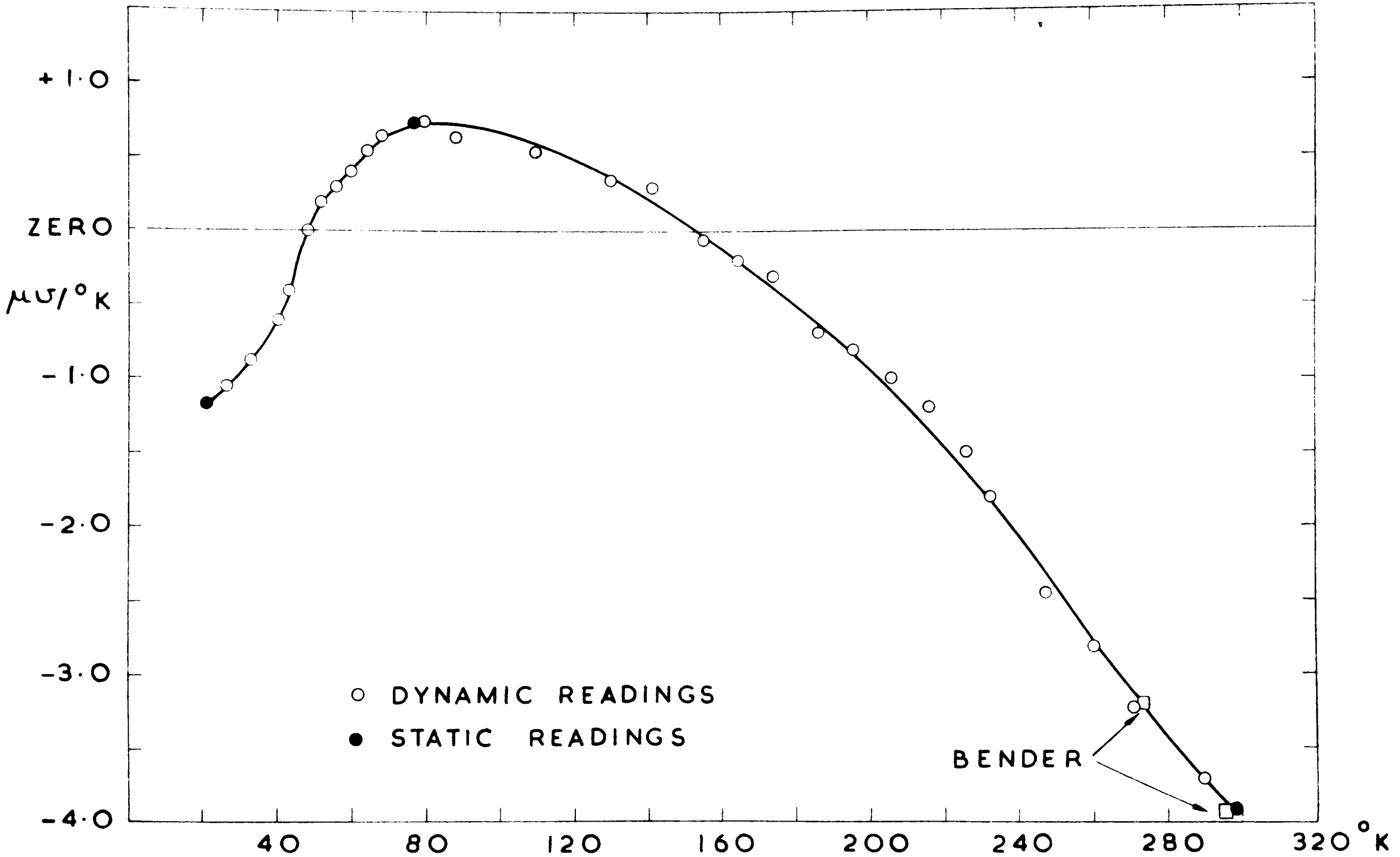


FIG.4.2. THERMOELECTRIC POWER OF Th 4

to make use of commercial-grade, oxygen-containing copper, for in this the undesirable effects of any iron present would probably be completely inhibited.

It is interesting to observe that several workers in the past have taken copper as an absolute standard of thermoelectric power. Potter (1941), for instance, who determined the thermoelectric power of a number of transition metals at several fixed temperatures down to 20°K, compared his powers with that of silver, having initially standardised his silver against copper. Presumably, he made use of Borelius' table for copper. Again, Tyler, Wilson and Wolga (1953), who measured the thermoelectric power of uranium against copper at temperatures above 20°K, stated that they used Borelius' values. That is, they assumed the thermoelectric power of their copper to be identical to that of Borelius', even at 20°K. This is unjustified, and we will show (section 4.3) that Tyler, Wilson and Wolga's curve for uranium becomes similar to ours if this assumption is not made.

4.2. Thorium.

Details of the two samples studied, Th 4 and Th 5, have already been given in section 3.1.

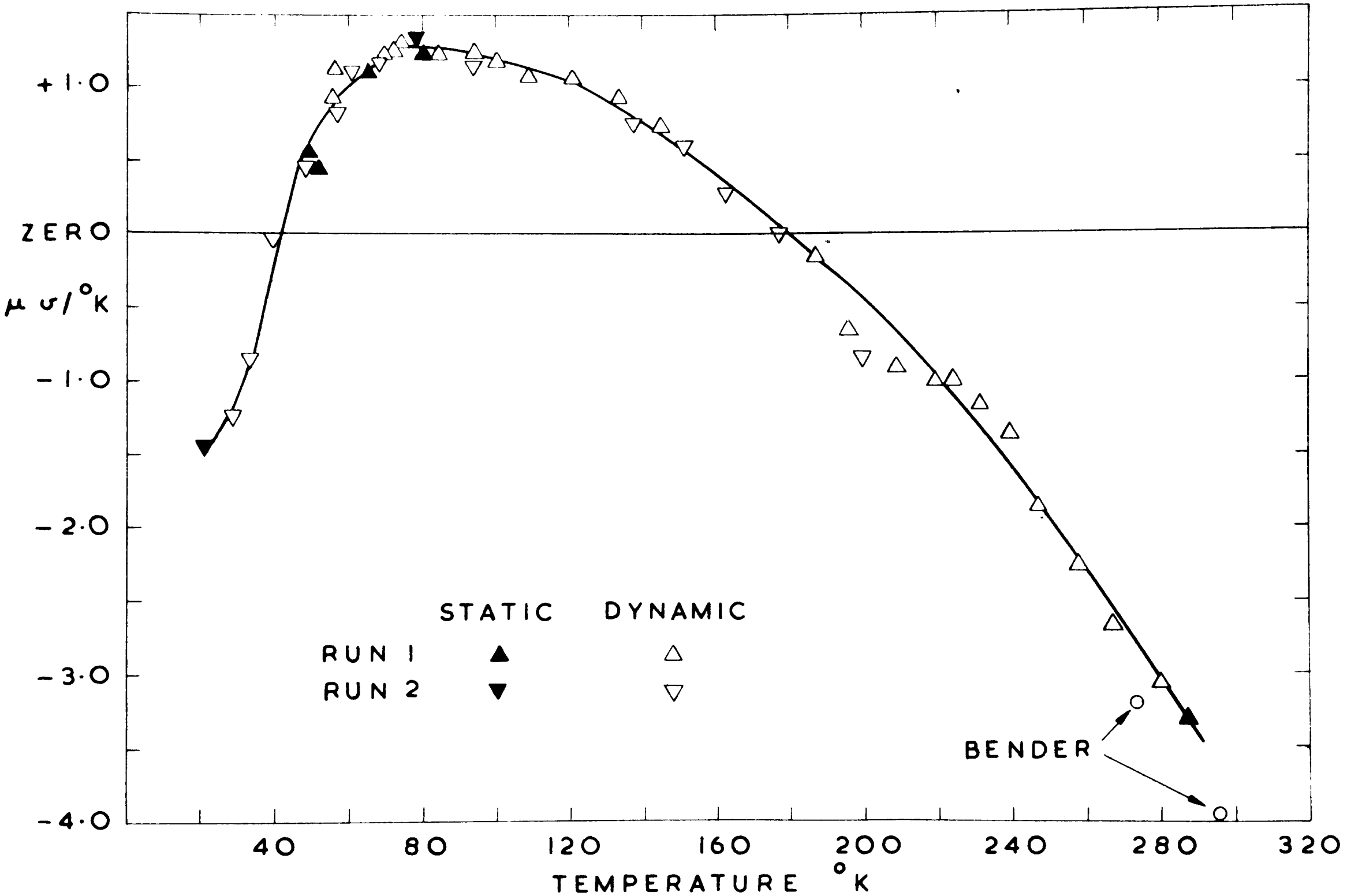


FIG. 4.3. THERMOELECTRIC POWER OF Tb 5

No previous work on the thermoelectric power of thorium has been done below room temperature. Above room temperature, the thermoelectric power has been measured by Bender (1949) and Thompson (1933) who gave results relative to platinum up to 1000°C, and Bodine (1956) whose measurements were limited to the temperature range 400 to 1100°C. Employing reasonable values for the absolute power of platinum at 273 and 295°K, we obtain for the thermoelectric power of thorium from Bender's data at these temperatures ~ -3.2 and -3.95 microvolts per °K respectively. These points have been included on our graphs (fig. 4.2 and 4.3) for comparison.

As explained in section 2.9.3, our experimental points were of two kinds: those obtained statically under equilibrium conditions of temperature, and those obtained dynamically while the specimen as a whole was changing its temperature (usually warming). We have distinguished between such static or dynamic values on all our graphs, and it will be observed that, in general, the curves obtained dynamically do pass through the points found statically. This indicates that nearly equilibrium conditions were continuing to be met with on the dynamic runs.

Between runs 1 and 2 on Th 5, the specimen was

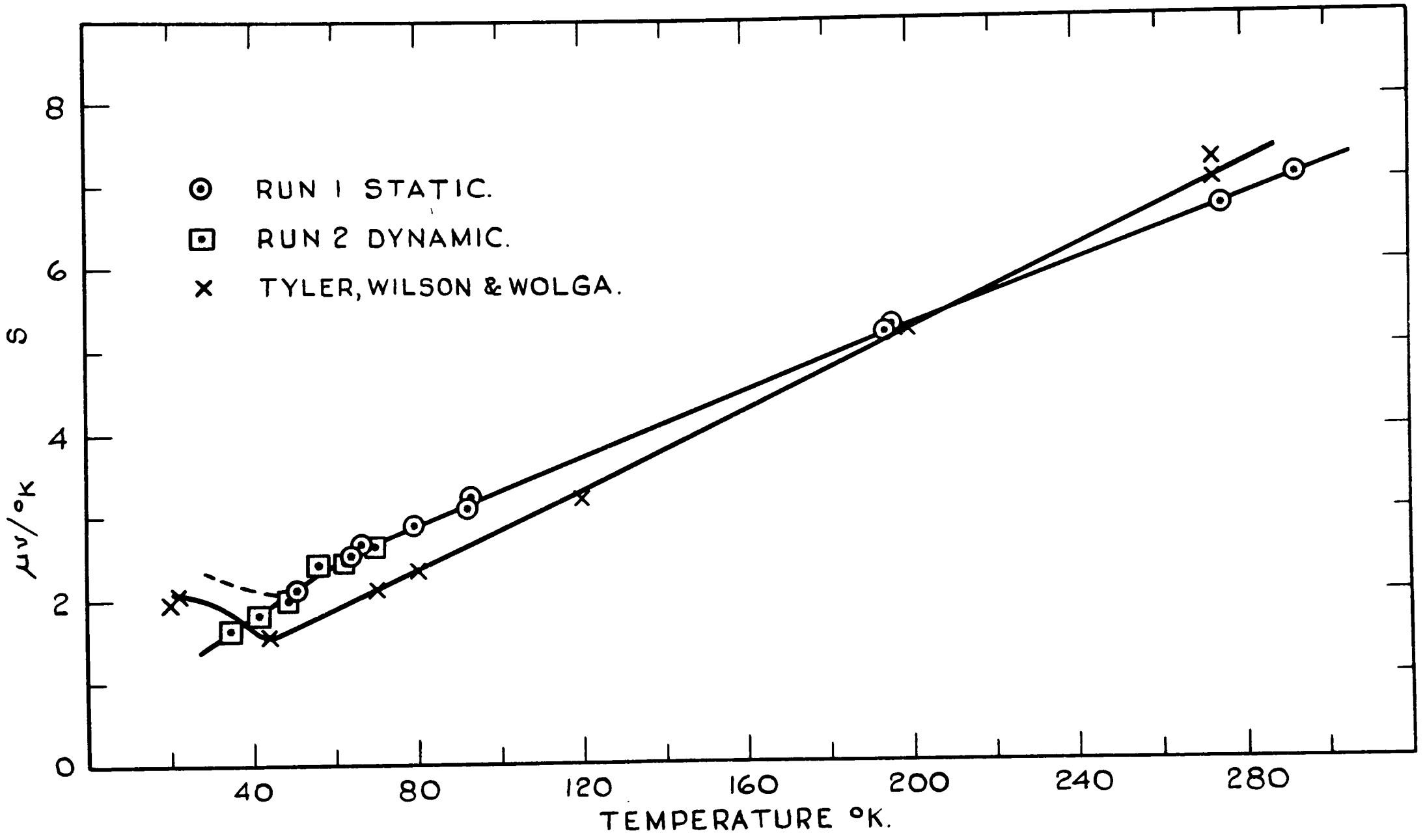


FIG. 4.4 THERMOELECTRIC POWER OF URANIUM.

completely unmounted, the thermocouples being unsoldered and the copper rings removed, and then remounted once again with the rings this time a different distance apart. This was done to check that the results obtained were not dependent on the manner in which the specimen was mounted.

4.3. Uranium.

Full details of the specimen studied (U2b) can be found in section 3.2.

The results of static and dynamic runs are presented in fig. 4.4, together with the graph of Tyler, Wilson and Wolga (1953). These authors, also, employed a differential method.

It is seen that our curve is linear from room temperature down to about 50°K, at which temperature there is a change of slope. Tyler, Wilson and Wolga's curve, too, is approximately linear down to the same temperature, but in this case there appears to be a minimum at 45°K and a maximum at 25°K. It will be recalled (section 4.1) that these authors made use of Borelius' data for the thermo-electric power of copper when evaluating their results. If instead we employ Borelius' data for copper, then our curve also turns upwards (hatched line, fig. 4.4) in a

similar way. This suggests that the readings of Tyler et al. are in error at 20°K, so that, instead of a minimum in the thermoelectric power of uranium at 45°K, there is merely a change of slope. As indicated in section 3.2.2, the anomalies in the Hall coefficient and electrical resistivity occur near to this temperature.

Measurements of the thermoelectric power above room temperature have been made by Dahl and van Dusen (1947) and by Costa (1960). Their published values were given relative to the thermoelectric power of platinum, which had therefore to be allowed for when obtaining the ice-point values presented in Table 15.

TABLE 15.

S_u at Ice-Point in μv /°K		Method
Dahl and v.Dusen (1947)	~ 7.6	Integral
Tyler, Wilson and Wolga (1953)	7.1	Differential
Costa (1960)	~ 5	do
Present work	6.65	do

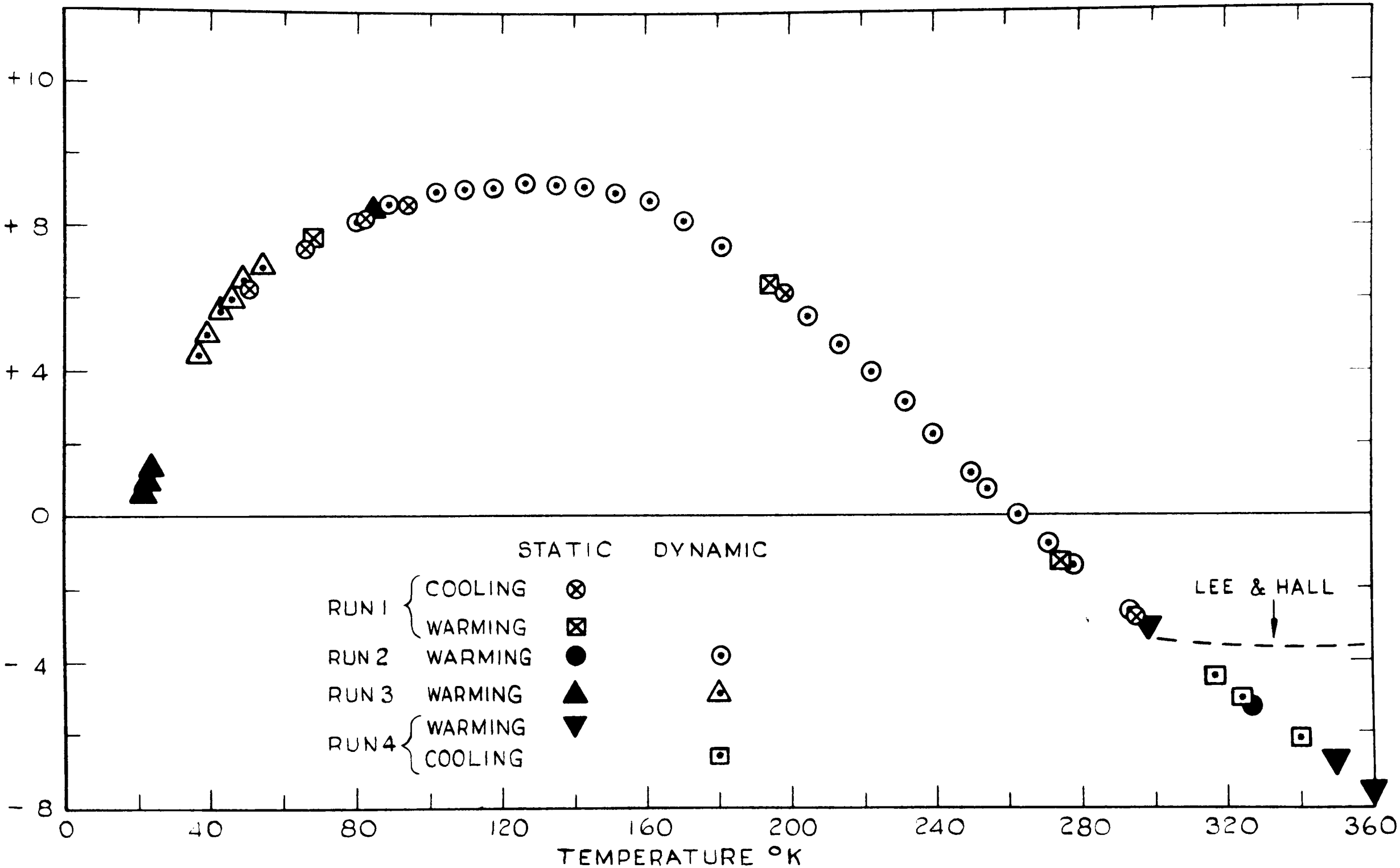


FIG. 4.5 THERMOELECTRIC POWER OF NEPTUNIUM.

4.4. Neptunium.

For details of the sample studied (Np 3) reference should first be made to section 3.3.

The only material that was available for investigation was our previous neptunium specimen, Np 2. It was therefore arc-melted once again, and then extruded as a 0.040 in. diameter rod. Neptunium, like the other actinides, is extremely brittle and, on being extruded, it broke several times. The longest piece, in fact, was only 15 mm. in length. It was decided to make use of this short rod, however, as no more specimens could be prepared for some considerable time. Thus the greatest distance apart of the thermocouples that could conveniently be managed was only 9 mm, and systematic errors from incorrect ΔT measurement are therefore likely to have been greater in this specimen than in any of the others. ΔTs of the order 2 to 4°K were obtained and used throughout.

The results of our runs can be seen in fig. 4.5, in which some of Lee and Hall's data have also been included. The latter measured the thermoelectric power between 300 and 850°K by an integral method (Lee, Evans, Hall and King, 1959). Though our room temperature value was very similar to theirs, we immediately found that the slopes

of the S-T curves at room temperature were widely different. We thereupon carried out a run to higher temperatures (360°K) in order to extend the range over which our results could be compared with Lee and Hall's.

The difference between the two curves merely increased still more, and at 360°K was far too large to be explained by the use of differing techniques*, despite our smaller specimen. The specimen used by Lee and Hall had been cast, and it is possible that inhomogeneities caused by imperfect casting could have affected the thermoelectric power appreciably, because of the enormous temperature gradients necessitated by the integral method in such a short specimen (4 cm. long). But again it must be recalled that agreement on the thermoelectric power of plutonium was good between us. It is instead more likely that, even though both specimens came originally from the same source, the true explanation lies in differing purities, since it is well known that the thermoelectric power is one of the most purity sensitive of all properties. In point of fact, the specimen on which Lee and Hall did their experiments was our Np 1 (section 3.3) and, as was fully discussed in section 3.3.2, this was subsequently shown by

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* Cf. fig.4.6. Our results on Pu compare well with Lee and Hall's.

susceptibility measurements to be ferromagnetic at low temperatures. Our Np 2 on the other hand, from which our Np 3 was later manufactured, did not display such magnetic behaviour. It is therefore probable that our data is more representative of pure neptunium than Lee and Hall's. It should nevertheless be remembered that the purity of the original material from which both specimens were made was only 99 weight per cent.

The data obtained by us, both statically and dynamically and on warming and cooling runs, agreed well with one another, with no suggestion of any hysteresis.

Notwithstanding all that has been said before, we must point out that our graph displays a slight change of slope at about 275°K i.e., close to the temperature of the upper resistance anomaly in Np 1.

4.5. Plutonium.

The specimen investigated (Pu 5) was a cast rod, obtained originally from the same billet of plutonium as Pu 3 (see section 3.4). It was not very well cast, for it contained a few surface pits and possibly holes, which would account for the rather low density of the cast rod compared with the original material.

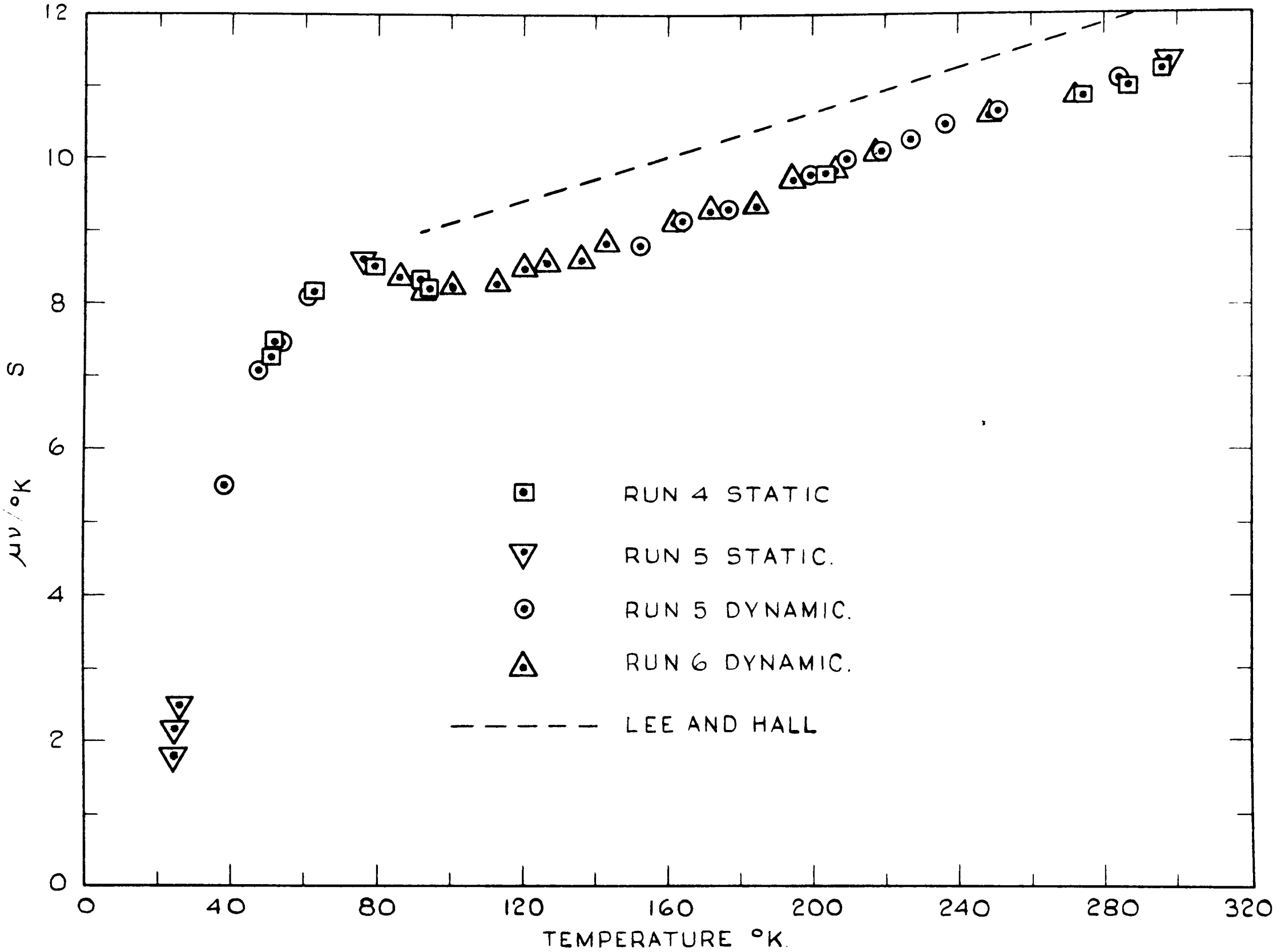


FIG. 4.6 THERMOELECTRIC POWER OF Pu.

The results of our runs appear in fig. 4.6. Previous work on the thermoelectric power of plutonium is limited to that of Lee, Evans, Hall and King (1959) between 20°C and 630°C (integral method) and Costa (1960) between 20°C and 580°C (differential method). Lee and Hall had also done one run from 95°K upwards (unpublished) and their measurements have also been included in fig. 4.6.

We notice at once that both their curve and ours have almost the same slope over the common temperature range above 100°K. Our room temperature value of 11.2 microvolts/°K, however, comes nearly 10% lower than Lee and Hall's figure of 12.1. By contrast, Costa's room temperature reading was ~12 microvolts/°K at the start of his first run, but only ~7 on succeeding runs. This was probably due to the thermal cycling through the α, β and γ phases, or possibly to a diffusion of platinum from his thermocouples at high temperatures. The room temperature value of the thermoelectric power quoted in Lee, Evans, Hall and King's paper was as high as 16 microvolts/°K.

It will be seen that the point at which linearity of the thermoelectric power with temperature breaks down is ~100°K, the temperature of the resistivity maximum.

Perhaps we should also mention that agreement of data taken on warming and cooling runs was good. No hysteresis was observed after cooling to either 77 or 20°K and then returning to room temperature once more.

CHAPTER 5.

Further Discussion of the Results

The purpose of this Chapter is to hold further discussions on some of the individual problems already encountered, and to discuss the various properties of the actinide metals so far as they relate to our investigation.

5.1. General.

The electrical resistivities of the four actinide metals investigated were all very high, being of the same order of magnitude as the rare earth and transition metals. These latter metals possess the common feature of incompletely full inner shells. With the transition metals of the first, second and third long periods, it is the 3d, 4d and 5d shells respectively that are incomplete; whereas with the rare earths it is the 4f shell that is being progressively filled on passing along the series (the 5d shell, at the same time, being incomplete). The actinide metals in their turn are believed to behave in a manner similar to the rare earths, the shells concerned being the 5f and 6d ones.

Now it is typical of all of these elements that they have high values for the electrical resistivity and for

the electronic specific heat, compared with the common monovalent and divalent metals. Moreover, they have strong paramagnetic susceptibilities and some of the transition elements and rare earths are ferromagnetic or antiferromagnetic over certain ranges of temperature. It is generally accepted that these properties are consequences of the incomplete inner d- or f-shells and, at least in a crude qualitative manner, their behaviour is now understood.

Thus, the high resistivity of the transition metals was explained by Mott (1936) on the basis that the very large scattering of the conduction electrons was due to interband transitions. He supposed that the valency electrons were shared between a broad, low density of states s-band and a narrow, high density of states d-band. This high density of states arises because the spatial extension of the d-electron wave functions is much less than that for the s-electrons, with consequently less overlap from atom to atom. The d-band is therefore narrower, and yet has to accommodate ten electrons compared with the s-band's two. Because of this, the d-band electrons contribute very little to the conductivity, their effective mass being so large. The d-band nevertheless

plays an important part in the resistivity since the conduction (s-) electrons can be scattered, not only into energy levels in the s-band, but into vacant states in the d-band. Since the density of the latter is so high, these s-d transitions will add greatly to the scattering probability and thus to the resistivity.

This picture applies equally well to the rare earths, and to the actinides also. However, in the latter the electronic properties should be associated with the overlapping energy bands formed from a mixing of 5f and 6d states. Wigner-Seitz calculations by Lehman (1956) (and Ridley (1958) for U) have shown that, for these metals, the 7s band lies several electron-volts above the Fermi level and is therefore unlikely to be occupied at all in the metal.

The actinide metals with which we have been concerned, viz. Th, U, Np and Pu, will now be discussed in turn.

5.2. Thorium.

Thorium has four electrons outside the closed shells $1s^2\ 2s^2\ \ldots\ 5d^{10}\ 6s^2\ 6p^6$, and was the simplest of the metals studied. Spectroscopic data suggest that in the free atom the 5f atomic energy levels are unoccupied,

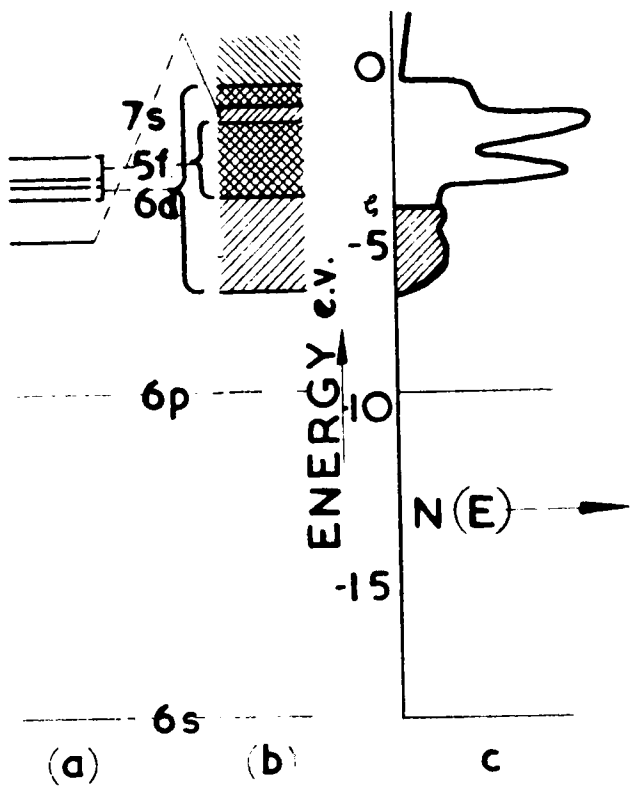


FIG. 5·1. LEHMAN'S BAND PICTURE OF Th.

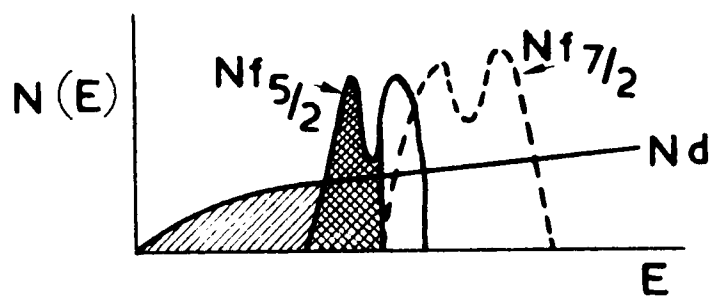


FIG. 5·2. LOMER AND RIDLEY'S BAND PICTURE OF U.

since they are higher in energy than the 6d and 7s levels. The outer electronic configuration is therefore most likely to be $6d^2\ 7s^2$.

Lehman (1956) has obtained an energy band scheme for f.c.c. thorium, and this is shown in fig. 5.1(b), together with the corresponding density of states curve (c). The splitting of the 5f and 6d states by spin-orbit interactions is important in all of these metals, where narrow bands are involved, and Lehman found that for thorium the 6d levels were separated by 0.4 eV and the 5f by 0.7 eV. On forming the solid, the 5f, 6d and 7s levels spread out into bands, the 7s band being raised in energy by several electron-volts. The 6d levels form broad, overlapping bands, while the 5f levels form much narrower ones as a consequence of the more limited spatial extension of the 5f electronic wave functions (the 5f electrons, being inner shell electrons, they are less strongly influenced by the crystalline field). The still lower-lying 6p, 6s, etc. shells are essentially unaltered. The filled portion of the band system is indicated by the shaded region in fig. 5.1(c). This is sufficient to contain four electrons per atom, viz. the two 7s and the two 6d electrons from the neutral atom.

Additional evidence that the bottom of the 5f band lies above the occupied region of the 6d band lies in the lack of an unusually large electronic specific heat (Smith and Wolcott (1955), Wallace, 1960), such as there is in uranium, and in a much lower electrical resistivity. Both of these are proportional to the density of states at the Fermi level, a high value of which signifies a high electronic specific heat and high resistivity. Also, from equation (16) (next section), the fact that the thermoelectric power of thorium at room temperature or above is much smaller than in the other actinides suggests that the slope of the density of states curve at the Fermi level is smaller as well.

Thus it is considered that both the 5f and the 7s states are unimportant in metallic thorium, and that the 6d states are the conduction states.

We might also point out that the electrical resistivity, besides being so much lower than in the succeeding actinides, has an almost normal temperature dependence (fig. 3.1). Above $T \sim \Theta/4$ and up to room temperature, it was quite linear and did not display the decreasing temperature coefficient found in uranium and neptunium and which is characteristic of many transition metals at high temperatures. This is not to say that it

would not have set in at higher temperatures in thorium as well. The appearance of this effect, however, according to the explanation of Jones (1956) requires a density of states that is varying rapidly with energy in the neighbourhood of the Fermi surface. This will be discussed fully in the next section.

5.3. Uranium.

The ground state of the neutral uranium atom according to the spectroscopic data of Keiss, Humphreys and Laun (1946) is $5f^3\ 6d\ 7s^2$. It has been shown by Ridley (1958) and Lomer and Ridley (1958) that, as in thorium, the 7s states are higher in energy in the metal than in the free atom and are not likely to be occupied. The 6d states were found to spread out to form a broad band 6 eV wide, the wave function being nearly uniform over most of the atomic cell, while the 5f wave function was fairly compact giving a narrow band 1/2 to 1 eV wide. The density of states represented by this band picture is illustrated in fig. 5.2. The f-band has about the same energy as the d-band, overlapping it such that there are about three electrons in each. Spin-orbit interactions split the f-band into two parts; the six states that form the lower energy band have $j = 5/2$ and

the remaining eight have j = 7/2.

This band model is not unlike that of Friedel (1956), who also supposed there to be a narrow, high density band overlapping a broad, conduction band. However, his conduction band is based on 7s, 7p electrons instead of 6d, and his narrow band on 6d-5f hybrids instead of on mostly 5f electrons. Unfortunately, he gives no numerical calculations to support the use of 7s, 7p electrons in his theory, and Lehman (1956, 1957), who has also done some band calculations on uranium, criticises him for this and for the neglect of spin-orbit effects. Lehman, like Ridley, had found that the 7s band lay above the Fermi level.

That the occupied region of the 6d band, in contrast to thorium, probably overlaps the 5f band comes from the very much higher density of states at the Fermi level which is indicated by various experimental data. For instance, the specific heat which has the Dulong and Petit value of ~6 cal/mole/^{o}C at room temperature doubles on raising the temperature to 650^{o}C (Ginnings and Corruccini (1947), North, 1952). The large electronic contribution was also seen in Smith and Wolcott's (1955) low temperature measurements, which gave an electronic specific heat coefficient of $\gamma = 26.10^{-4}$ cal/mole/deg^{2}.

For thorium, they had found γ to be $11.2.10^{-4}$.

The electrical resistivity measured at room temperature is also considerably larger than that of thorium (roughly double), but more important is the fact that the resistivity is not exactly proportional to T, for from even quite low temperatures ($\sim 100^{\circ}K$) the temperature coefficient very slowly decreases with increasing temperature. Dahl and van Dusen (1947) found that at much higher temperatures the deviation rapidly became more and more serious, the temperature coefficient having fallen by a half at $800^{\circ}K$. This behaviour has been explained by Friedel (1956) by way of an increasing Debye Θ with temperature, which lowers the resistivity through the formula $R \propto \frac{T}{M\Theta^2}$ (an equation that can be derived from simple considerations - see Mott and Jones for example). Friedel imagined the increase in Θ_D to be caused by a gradual rearrangement of the atoms of the lattice as a result of certain covalent bonds weakening with rising temperature.

The explanation put forward by Chandrasekhar and Hulm (1958) however makes use of a band model for uranium of the type we have been discussing. Their analysis has the further advantage of explaining qualitatively their

results on the electrical resistivity of b.c.c. U-Mo and U-Nb alloys. The approach they used is based on that originally put forward by Mott (1936) to explain the departure of the ρ-T curves of Pd and Pt from linearity at high temperatures. Recently, this has been discussed more generally by Jones (1956), and applies to a metal in which the electrons can be regarded as occupying two overlapping bands, one of which has a high and the other a low density of states. We will follow Blatt (1961) in not specifying exactly which electrons occupy each band, but will call the broad, low band the conduction (c-) band and the narrow, high band the f-band (the f-states being the final states for the scattering processes which limit the conductivity).

The conductivity equation $\sigma = \int_0^\infty \sigma(E) \left(-\frac{df_0}{dE}\right) dE$

where $\sigma(E)$ is given by equation (5a), is a standard integral, and its solution can be found in Wilson (p.331). It is

$$\sigma = \sigma(\zeta) + \frac{\pi^2 k^2 T^2}{6} \left(\frac{d^2\sigma}{dE^2}\right)_\zeta + O(T^4) \qquad \ldots(14)$$

(Again we are using the symbols of Wilson and of Mott and Jones).

Since the density of states within a high narrow band alters sharply with change in energy, the dependence of

the Fermi energy on temperature is important. Calculating the effect that this temperature dependence has on $\sigma(\zeta)$ in (14), Jones (1956) obtained for the resistivity

$$\rho(T) = \rho(\zeta_o, T)\left[1 - \frac{\pi^2 k^2 T^2}{6}\left\{3\left(\frac{1}{N_f}\frac{dN_f}{dE}\right)^2 - \frac{1}{N_f}\frac{d^2N_f}{dE^2}\right\}_{\zeta_o}\right] \quad \ldots(15)$$

Thus the deviation of the resistivity from linearity with temperature is determined by the magnitudes of N_f and its derivatives with respect to E evaluated at the Fermi energy. Since, in the transition and actinide metals, N_f is a very complicated function of the energy, these metals might be expected to show such deviations, especially at high temperatures. Mott (1936), who assumed the f-band to be of standard form, accounted for the behaviour of Pd and Pt at high temperatures quite closely in this way.

The ρ -T behaviour of uranium is also explained quite satisfactorily in a qualitative way. Besides assuming $N_f(\zeta)$ to be large, we must also assume it varies rapidly with energy. These assumptions are quite in line with the band model we have been considering. Unfortunately without knowledge of the parameters involved, comparison with equation (15) cannot be carried further.

Blatt (1961) has extended Jones' analysis in order

to obtain related equations for the Hall coefficient and thermoelectric power as well. In a simplified form, his equation for S may be written

$$S = -\frac{\pi^2 k^2 T^2}{3e}\left(\frac{1}{N_f}\frac{dN_f}{dE}\right)_\zeta \qquad \ldots(16)$$

which is the same as Friedel's equation (6). (Friedel, 1956). Alternatively, this can be obtained by setting $\frac{1}{\sigma} \propto N_f(E)$ in equation (5), section 1.8. Then, with all due reserve for the present weakness of the theory of the thermoelectric power (as discussed in section 1.8), we may note that the experimentally determined positive S points to a positive value of $\left(\frac{dN_f}{dE}\right)_\zeta$. This agrees with the position of the Fermi level on Friedel's and Lomer and Ridley's band schemes.

Returning to the anomalous variation of resistance once more, we should point out that there is likely to be still another temperature dependent mechanism operating. This is the thermal expansion which, by <u>decreasing</u> Θ_D with rising temperature, should cause the resistance to increase more rapidly than would be expected from $\rho \propto T$. Friedel considered that in uranium this would more than compensate for the lowering expected from equation (15); and is the reason why he hypothesised that Θ_D in fact

increases with temperature as a result of a weakening of covalent bonds. However, an extension of equation (15) by Chandrasekhar and Hulm to include alloys (see later, section 5.6) enabled them to account qualitatively for their results on γ-uranium alloys, and this has been further analysed satisfactorily by Blatt. This model has a lotfor which it can be commended, and we feel that it probably is, in fact, sufficient to explain the observed resistance of uranium. We shall have more to say on this kind of resistance behaviour in the following sections.

5.4. Neptunium.

Neptunium has seven electrons outside the radon core. The outer electronic configuration of the neutral atom, according to atomic beam experiments, is $5f^4\ 6d\ 7s^2$, but there is no supporting spectroscopic evidence as yet (to the writer's knowledge).

It is probable that the band structure of α-Np is similar to that of α-U, namely a broad, low conduction band overlapped near the Fermi surface by a narrow, high density of states f-band. This f-band would be based on 5f electrons or mixed 5f and 6d electrons.

The electronic specific heat is evidently even larger than that of U (Evans and Mardon, 1959) and the

paramagnetic susceptibility is also large (Gardner, priv. comm.). The placing of the Fermi surface within the high density f-band seems to be justified by these high values and by the extremely high electrical resistivity. With regard to the latter, for a metal with (comparatively) such a low residual resistance, the room temperature value is one of the highest met with in the entire periodic table. Indeed, only Pu (148 $\mu\Omega$ cm), manganese (147 $\mu\Omega$ cm, White and Woods, 1957) and gadolinium (127 $\mu\Omega$ cm, Colvin, Legvold and Spedding, 1960) are higher. The value of 121 $\mu\Omega$ cm is four times that of U, and the decrease in the temperature coefficient of resistance with increasing temperature even more striking (figs. 3.10, 3.11), for it eventually becomes <u>zero</u> as the α-β phase change is approached. The same mechanism as that discussed for uranium may be operating here also, since a high value of $(dN_\zeta/dE)_\zeta$ again seems likely. Alternatively, it is possible that the band structure itself may be temperature dependent, giving rise to an anomalous variation of the density of states with temperature, or to promotion of electrons into the conduction band. The low temperature coefficients of β- and γ-Np are possibly related to those of Pu (see section 5.5.5).

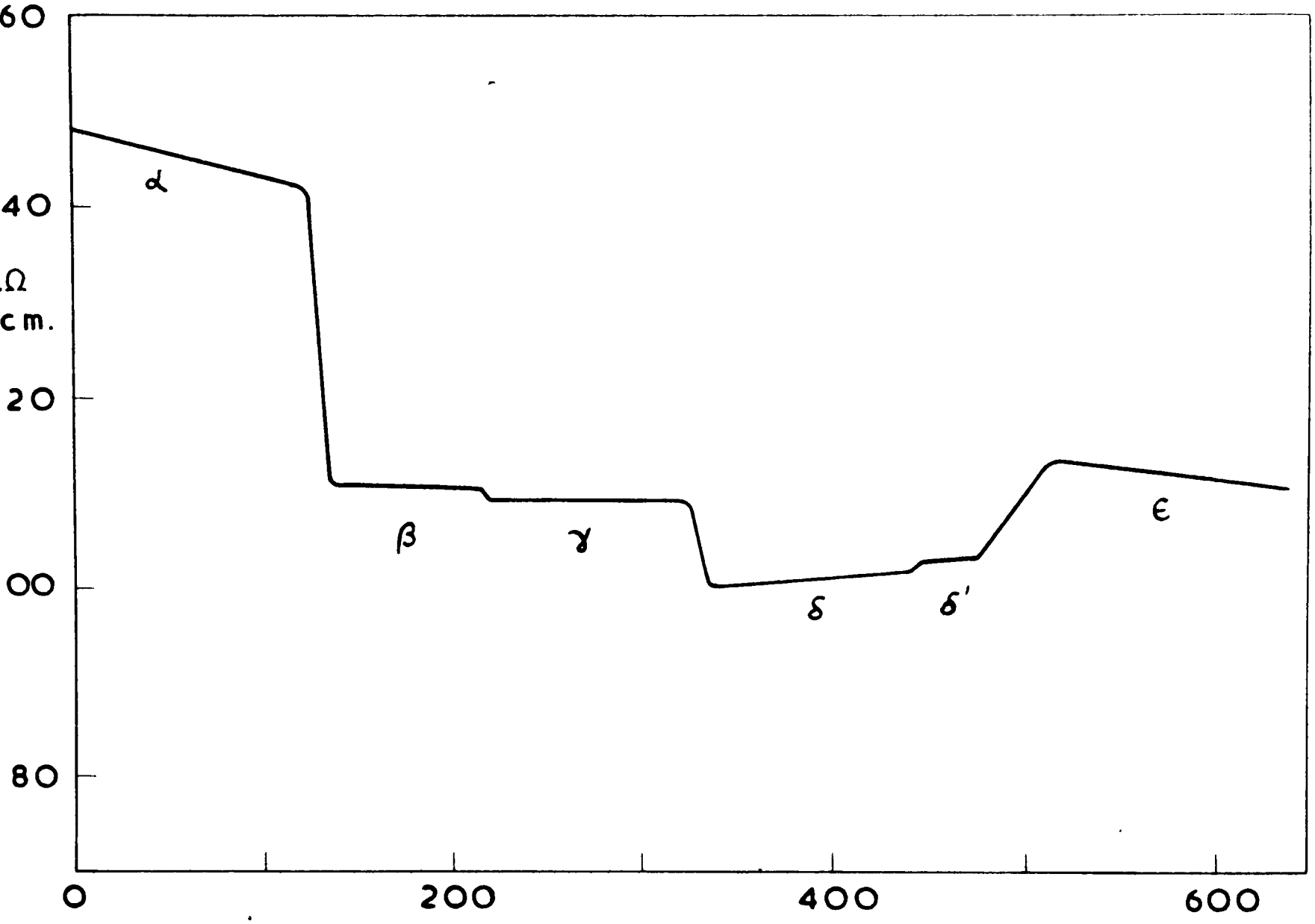


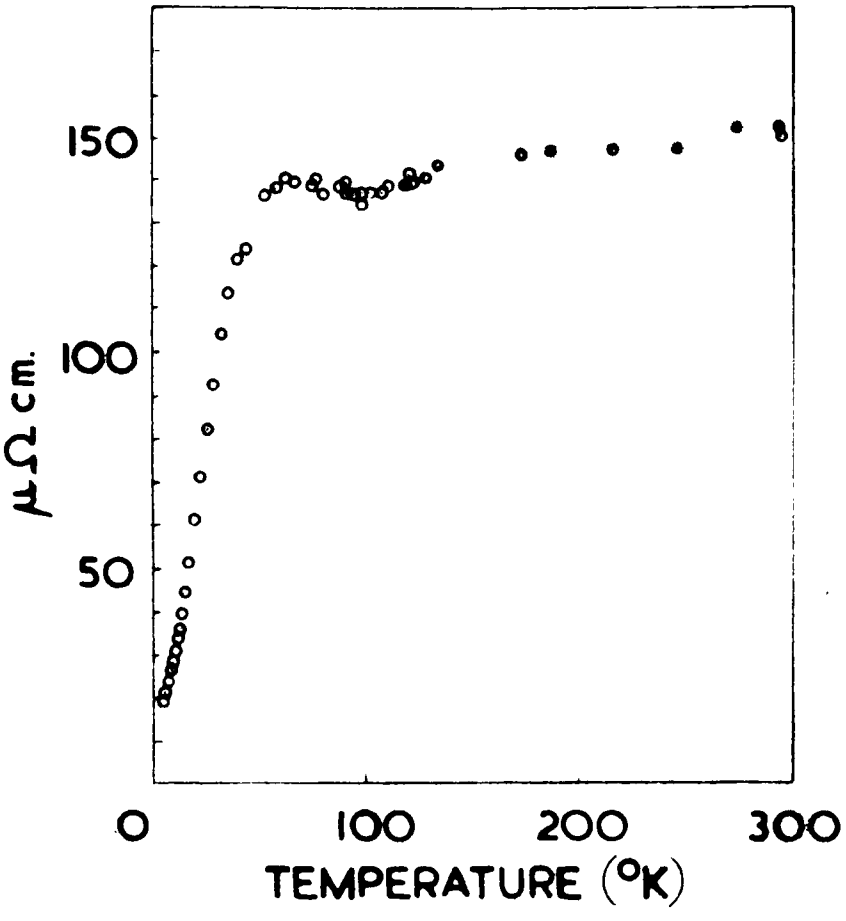
FIG. 5·3. ELECTRICAL RESISTIVITY OF Pu ABOVE ROOM TEMPERATURE (KING, UNPUBL.)

5.5. Plutonium.

The spectroscopic data of van den Berg and Klinkenberg (1954) indicate that the ground state of the neutral Pu atom is probably $5f^5\ 6d\ 7s^2$. As with the preceding elements, the work of Lehman (1956) suggests that the 7s states are not occupied in the metal. The band picture is probably again very like that of U, with the broad conduction band still containing about three electrons but the narrow band holding about five. Once again we have a very high electronic specific heat (Dean, Kay and Loasby, 1958) and paramagnetic susceptibility (Dawson (1954) for example), while the room temperature electrical resistivity is the highest of all the elements in the periodic table, having a comparable state of purity ($> 99.97\ \%$). We will now discuss the behaviour of the electrical resistance in some detail.

5.5.1. The resistance-temperature graph of Pu (fig. 3.19) has two outstanding features: firstly, the rapid fall in resistance below 105°K, and then, by way of contrast, the negative temperature coefficient existing above this temperature. As the graph at higher temperatures shows (fig. 5.3, King, unpubl.), the temperature coefficient remains negative as far as the α–β phase change at 390°K,

(a)



(b)

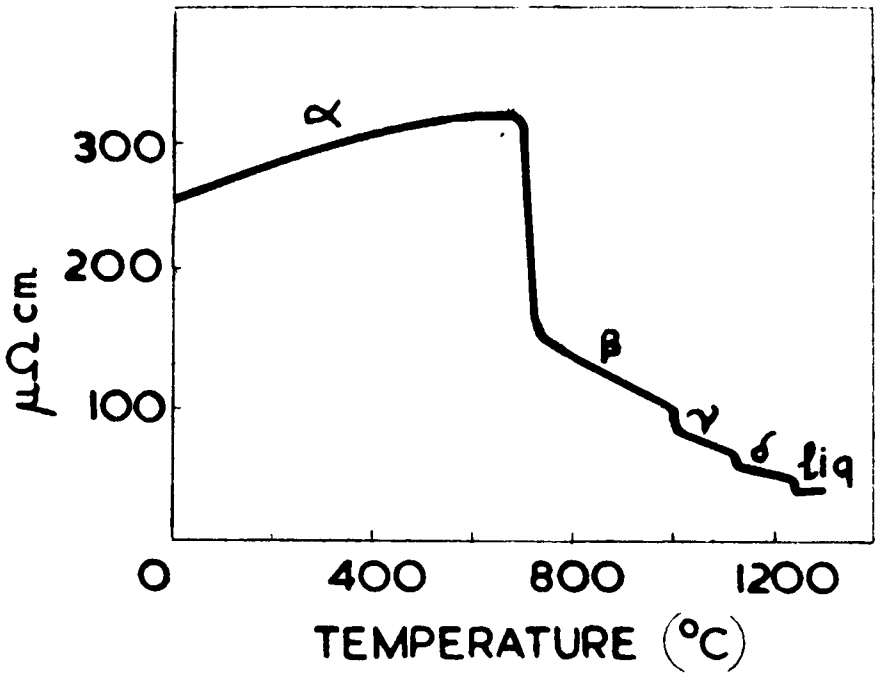


FIG. 5·4 ELECTRICAL RESISTIVITY OF MANGANESE.
(a) AFTER WHITE AND WOODS (1957)
(b) AFTER GRUBE AND SPEIDAL (1940)

and is negative in the β- and γ-phases as well. This behaviour is very similar to that of α-manganese, and before going any further we must see just how far the resemblance extends. The parallel is in fact quite close, and we feel that it should not be overlooked.

The only work below room temperature on the resistivity of α-manganese is that of White and Woods (1957) and their curve is shown in fig. 5.4(a). The close resemblance to that of α-Pu is at once apparent (cf. fig. 3.19). At higher temperatures the work of Grube and Speidal (1940), fig. 5.4(b), shows that the temperature coefficient is positive through most of the α-phase, but it does slowly decrease in magnitude with rising temperature and, in fact, becomes negative shortly before the first phase change at ~700°C. The temperature coefficient of resistance is negative in all three higher phases. As with Pu, the crystal structures of the α- and β-phases are very complex and have large numbers of atoms in their unit cells.

Now it has definitely been established by neutron diffraction that α-manganese is antiferromagnetic (Shull and Wilkinson, 1953). The temperature dependence of some of the additional low angle reflections indicated the Neel

point to be at ~ 100°K, i.e., at the minimum in the ρ-T curve and some 20°K above the broad peak which comes at 80°K. Associated with the Neel point is a small hump in the specific heat. It occurs at ~ 95°K (Shomate, 1945), and its magnitude is about 9% of the total specific heat at this point.

Because of the several resemblances existing between α-Pu and antiferromagnetic α-manganese, and for other reasons which we shall discuss shortly, we feel that α-Pu may well be antiferromagnetic too. Such discussion is necessarily rather tentative, for neutron diffraction experiments only can provide definite evidence for or against this hypothesis. At any rate we have not found, as a result of studying those physical properties that might possibly be influenced by the occurrence of antiferromagnetism, any evidence which is incompatible with this postulation.

5.5.2. The description of the anomalous resistance of α-manganese in terms of spin-disorder has been suggested by Coles (1958). On this model certain d-electrons are localised on particular atoms and are not spread out into a band. It is then supposed that there are exchange interaction effects between these electrons and the

conduction (s-) electrons; and that the energy of the interaction depends on the orientation of the spin of the conduction electron relative to the spin of the localised electron near which it is passing. It is then clear that the resistive component due to this cause should fall sharply upon ordering of the localised spins, and should become zero when all these spins are parallel. On the other hand, it should be a maximum when they are completely disordered. The picture is thus one of a sharply rising resistance to the Neel point, above which the spin-disorder term is constant, and the increase in resistance is solely due to thermal scattering. Broadly speaking, this is in agreement with experiment on α-manganese. The main difference is that the resistance rises more quickly than expected, and passes through a slight maximum about 20° below the Neel temperature, so that the latter comes at a minimum in the curve. It is possible that this effect is due to short-range ordering (Coles, 1958).

Qualitatively, the above model would explain the low temperature part of the resistance curve of Pu, if we assume there to be a Neel temperature at or rather higher than the temperature corresponding to the resistance

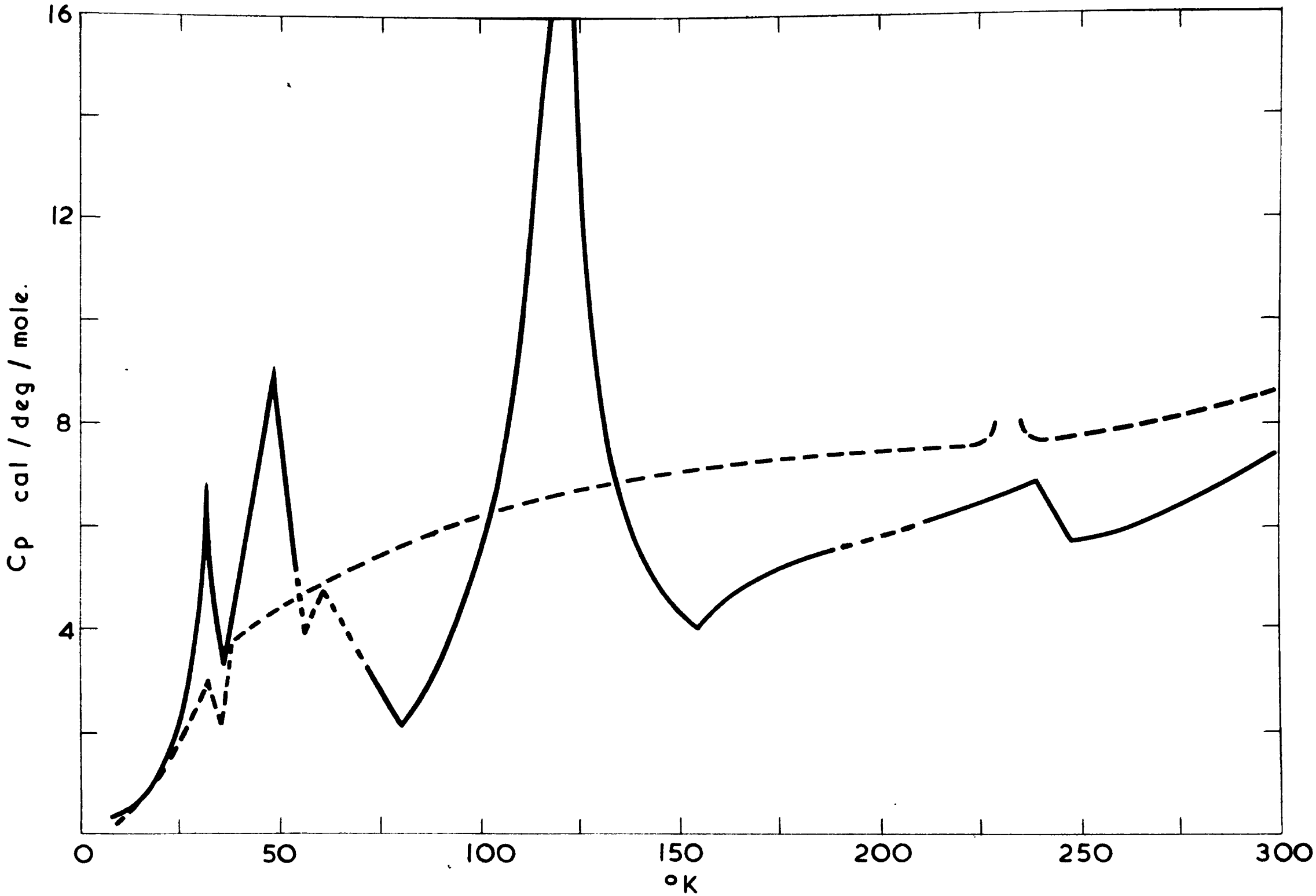


FIG. 5.5 SPECIFIC HEAT OF PLUTONIUM
(ACCORDING TO SANDENAW, OLSEN, AND GIBNEY)

maximum. The truly vast specific heat peak found by Sandenaw, Olsen and Gibney (1960) at 123°K (fig. 5.5) could be associated with this. The reality of their peaks, however, is in some doubt, since the first experiments of Loasby (priv. comm., 1961) above 50°K on almost identical material have shown no sign of any such anomalies*. Loasby says that the experimental difficulties and consequential errors are such that an anomaly of ~5% magnitude could have been missed. For our part, we had felt that, if the 123°K peak was really as large as that indicated by Sandenaw et al's work, its presence could probably be revealed by even a relatively crude experiment. We therefore did some thermal analysis warming runs on a 5 gm. Pu specimen, obtained from the same source as Sandenaw et al's. The specimen was thermally isolated as far as possible, so that it warmed mainly through its own production of heat. Stop-watch readings were then taken for 5 μv increases of the thermocouple (equivalent to 0.3 to 0.15°K) between 85 and 170°K. However, there was no evidence of any discontinuities

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* Loasby is using Pu from the same source as Sandenaw et al's, and he subjected it to the same kind of thermal cycling that these authors described.

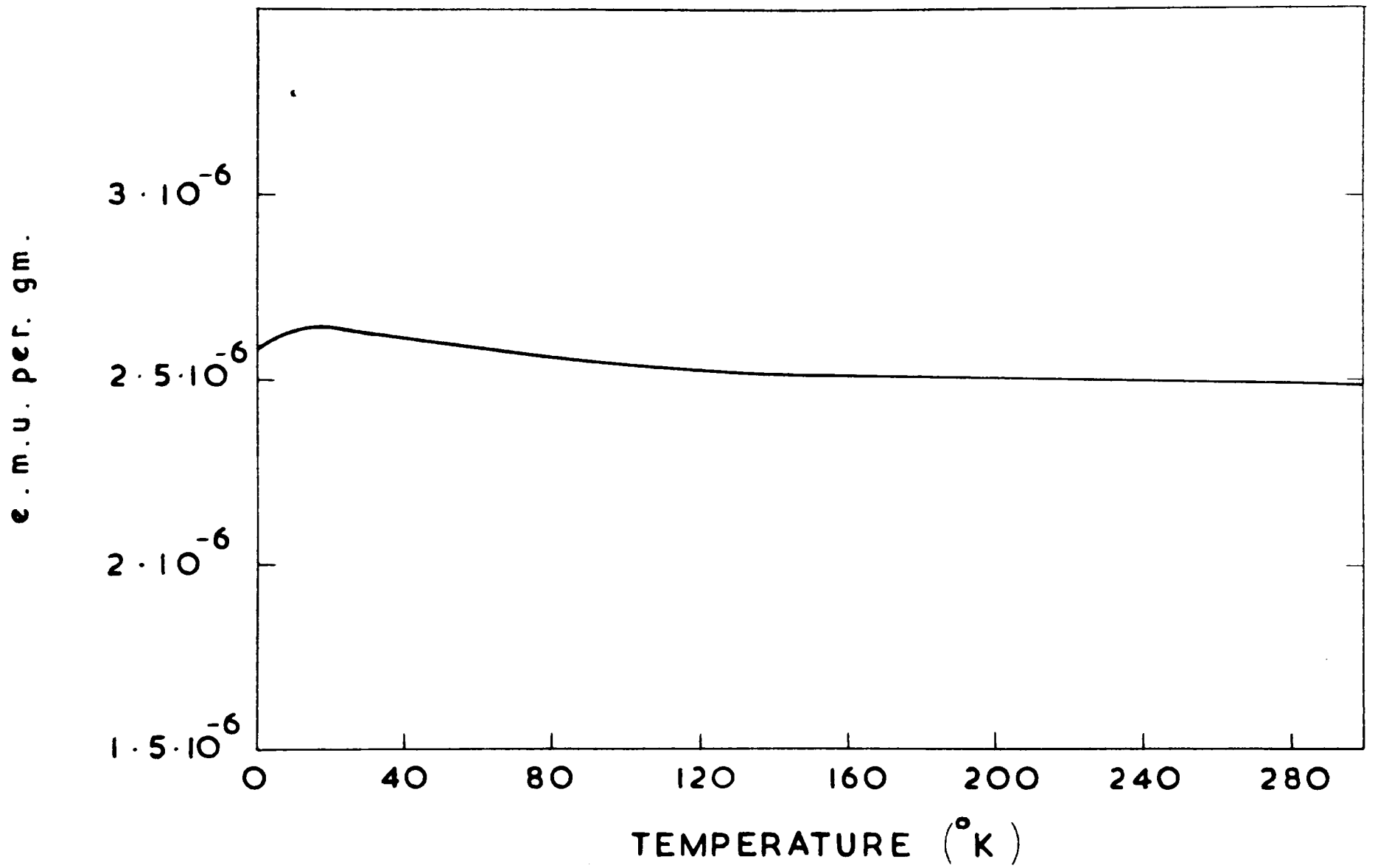


FIG. 5·6. SUSCEPTIBILITY OF Pu (WEIL et al. 1960).

in the slope of the graph, such as might have been caused by anomalous changes in the thermal capacity.

Turning to the magnetic susceptibility, it seems that no discontinuity at the supposed Neel temperature of Pu was found by either Dawson (1954) or more recently by Weil, Quezel, Cohen and Pascard (1960) on Pu of much better purity (fig. 5.6). A careful search in the region 100 to 150°K by Gardner (priv. comm.) has disclosed the presence of a very small anomaly though. The change in susceptibility was less than 1%, but it was nevertheless three or four times greater than the experimental scatter in this region. Experimentally, no anomaly in the susceptibility of α-manganese has been observed at or anywhere near the Neel temperature. While often in antiferromagnetic substances we expect to find an associated susceptibility peak (manganese oxide is typical), this is not always so, as was shown by Lidiard (1954). By assuming that the magnetically effective electrons were in non-localised states (collective electron approach) he found that in α-manganese any anomalies in the susceptibility or the specific heat due to the antiferromagnetic transition were very small, and certainly beyond the sensitivity of ordinary measuring equipment. Lidiard was apparently unaware of Shomate's

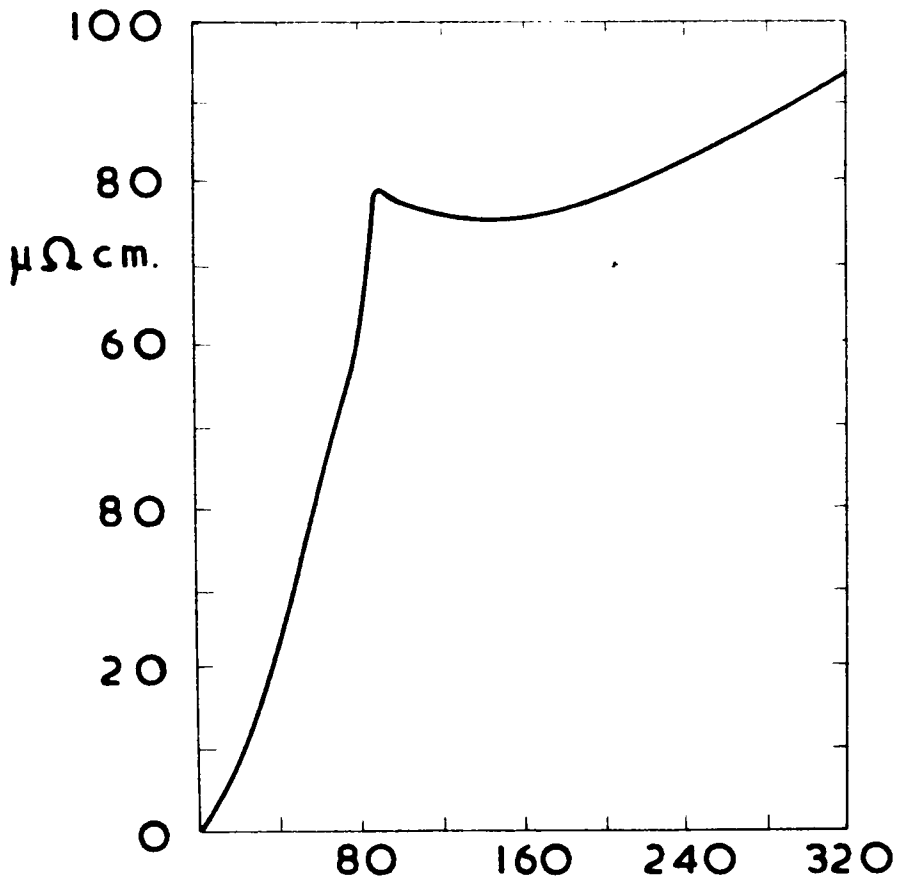


FIG. 5·7.(a) RESISTIVITY OF EUROPIUM.

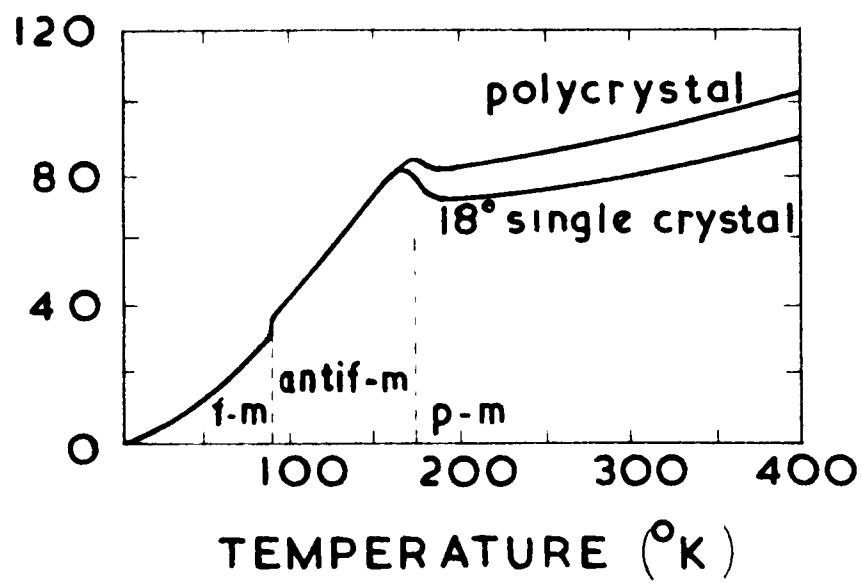


FIG. 5·7.(b) IDEAL RESISTIVITY OF DYSPROSIUM.

experimentally discovered specific heat peak, which is some one hundred times greater than that which he (Lidiard) deduced. Tredgold (1954) criticises Lidiard for this, saying that the discrepancy was due to the limitations of the collective electron approximation in its application to statistical treatments of exchange dependent phenomena. At any rate, we are able to conclude from the case of manganese that antiferromagnetism is not necessarily associated with a measurable anomaly in the susceptibility, but that it may nevertheless give rise to a measurable peak in the specific heat. Thus, the corresponding experimental data on Pu is not incompatible with the postulation of antiferromagnetism.

5.5.3. Many rare earth metals are antiferromagnetic over certain ranges of temperature, and some possess resistivity-temperature curves rather similar to that of Pu. Europium (at.no. 63) (Curry, Legvold and Spedding, 1960) and dysprosium (66) (Hall, Legvold and Spedding, 1960) are the best examples (see figs. 5.7(a) and (b)). The case of dysprosium is interesting because it demonstrates how the anomaly becomes more accentuated when a single crystal is employed. Dysprosium is antiferromagnetic between 175 and 90°K, below which it is ferromagnetic.

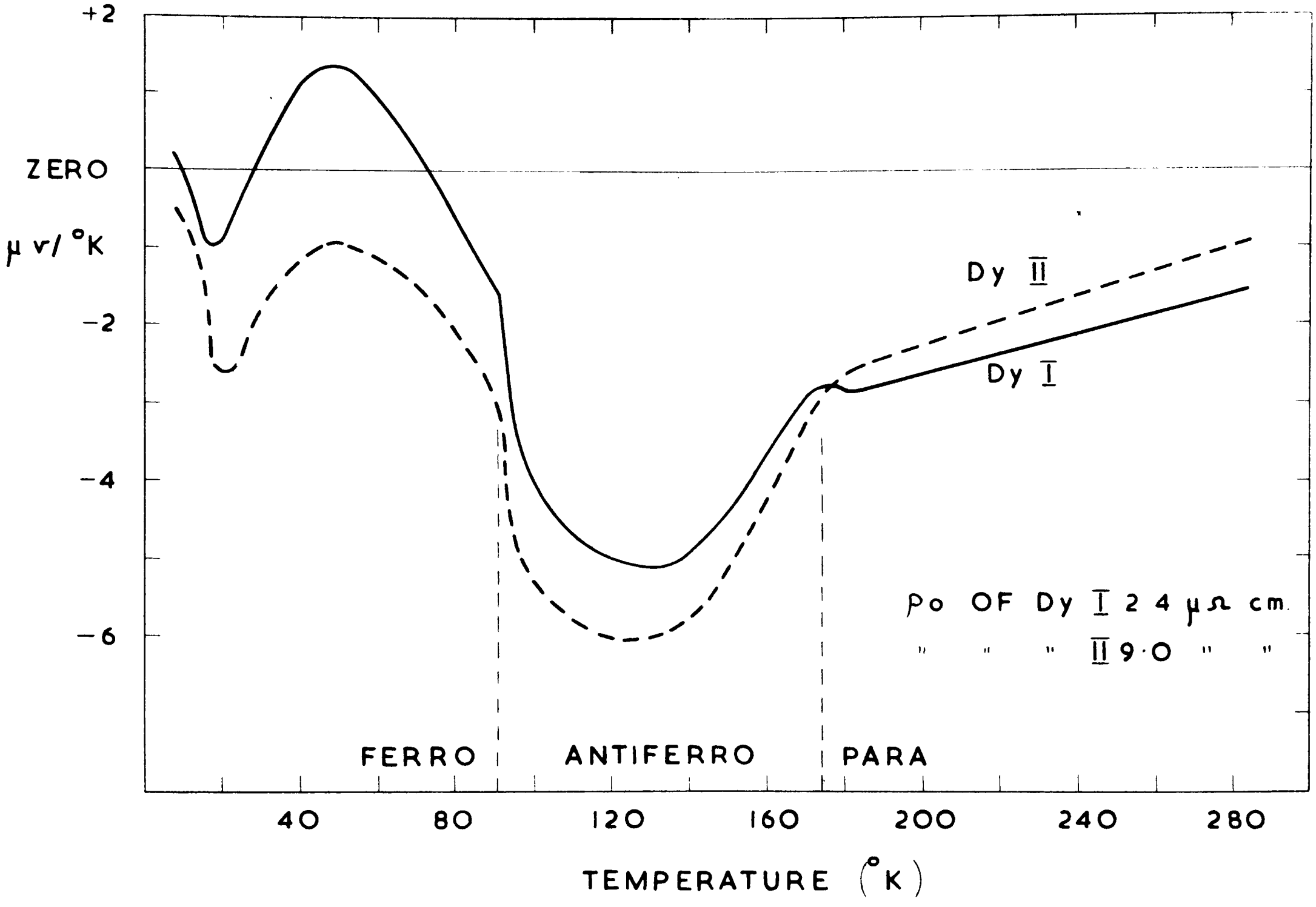


FIG. 5·8. THERMOELECTRIC POWER OF DYSPROSIUM (BORN, TO BE PUBL.)

The sharp peak in the resistivity of europium at 90°K occurs ~16°K below the Neel point, as found by la Blanchetais and Trombe (1956).

Of further interest is the as yet unpublished work by H. Born on the thermoelectric power of the rare earth metals. His graphs show the powers to be extremely complicated functions of the temperature, but they all possess the common feature of displaying marked changes of slope at magnetic transitions. We reproduce as an example Born's curves for dysprosium (fig. 5.8 - two specimens).

The thermoelectric power curves of Th and Np (figs. 4.2, 4.3, 4.5) are smoothly varying functions of the temperature. Pu, however, has an anomalous region between 60 and 100°K, in which a broad maximum at ~75°K is followed by a shallow minimum at ~100°K. The overall change in slope is very large, but this is rather different from any of Born's curves. The thermoelectric power of manganese, unfortunately, does not appear to have been measured, but chromium, which is also anti-ferromagnetic, has (Potter, 1941). The thermoelectric power of the latter is similar to Pu in that it rises extremely sharply from low temperatures, reaching a peak of 20 μv/°K at the Neel point at 308°K*, beyond which there

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* This is the value for the Neel temperature reported by Corliss, Hastings and Weiss (1959) from their neutron diff-

is a deep broad minimum before the power rises again.

Lastly, comparing the resistivity curves of Pu and manganese once more, we note that the variation of the "ideal" resistance of PuI_4 with temperature was as T^2 below 22°K (though the power index was rather higher (2.2 to 2.4) in PuI_3). This is about the same as that reported by White and Woods (1957) for manganese (2.0) below 20°K. As mentioned before (section 3.3.1), Baber (1937) ascribed this temperature variation in the transition elements to the effect of electron-electron interactions.

5.5.4. Residual Resistance of Pu.

We have indicated before (section 3.4.1) that the residual resistances of all the samples of Pu were extremely large, considering their high purities. Ratios of the resistance at 4.2°K to that at room temperature (295°K) of between 12 and 32% were obtained for the various specimens, despite (at times prolonged) annealing at elevated temperatures. Such high values are not uncommon amongst the ferromagnetic and antiferromagnetic rare earths. Also, White and Woods (1957) found the resistance ratios of two specimens of manganese to be ~7% and 11% respectively.

As pointed out previously (section 1.3), the residual resistance of metals arises from the presence of impurities in the lattice (particularly when in solid solution) and imperfections of the lattice, such as dislocations and vacancies. There are several reasons why Pu, in particular, should possess a highly strained lattice. Besides the effects of thermal cycling through high temperature phase transitions (pointed out in section 3.4) and the cold-work introduced by even low temperature thermal cycling (discussed at length in section 3.4.2), the lattice is continually undergoing internal radiation damage. As evidenced by the high self-heating, the internal bombardment due to its own α-particle production must be considerable. Such high energy particles, besides being imperfections themselves in the crystal, are the sources of other imperfections, since the effect of these particles is one of the creation of regions of very high temperature in the vicinity of their paths. Large numbers of phonons, electrons and actual lattice defects are therefore produced, and one might expect the resistance of plutonium to increase slowly with the passage of time because of the accumulating number of helium atoms and radiation damage. The time scale involved is, however, likely to

be quite long, and we did not find any significant change in the residual resistance when a run was done on Pu 3a after an interval of just a year.

Annealing Pu 5 in vacuo for 39 hours at 380°C (i.e. in the δ-phase) caused its resistance ratio to drop from 24% to 12%. This large decrease was probably due in part to annealing out of microdamage, though it is possible that, in addition, certain impurities were present which were less soluble in δ-Pu than in α-Pu and which had been driven out of solid solution. In antiferromagnetic metals the effect caused by the presence of impurity atoms (especially ferromagnetic atoms) in solid solution would be expected to be unusually large. Such impurities would inhibit perfect alignment of the antiferromagnetic spin system at low temperatures, the resulting disorder giving rise to an appreciable contribution to the residual resistance. Thus, if Pu was antiferromagnetic, this would account for the high and widely different residual resistivities found in the various specimens, and for the fact that the room temperature values were not so very different from one another. It will be recalled that, even though the residual resistivity of Pu 4 was over twice that of Pu 3, the resistivities at ρ_{max} were almost the same (Table 13). (Pu 4 was appreciably less pure than

Pu 3 (cf. table 12)).

Summing up our discussion on the low temperature behaviour of α-Pu, we can say that there appears to be much indirect evidence suggesting α-Pu to be anti-ferromagnetic, although as yet we have no real proof. For this, neutron diffraction studies would be necessary.

An alternative explanation of the anomalous resistance below 105°K is that it is due to an atomic order-disorder phenomenon. An ordering might be thought possible because of the complex crystal structure of the α-phase. However, δ-Pu shows the same kind of resistance behaviour as α-Pu and such an explanation will not do for this simple phase.

5.5.5. The other unique feature of the resistance behaviour of α-Pu is that over a considerable temperature range the temperature coefficient is negative. The factors which give rise to this are clearly great enough to balance out the contribution to the scattering from the lattice vibrations. In most metals the latter is the only temperature dependent scattering mechanism operating.

The origin of this anomalous behaviour may in part be related to the general tendency towards small temperature coefficients displayed by the preceding

actinides. There is certainly every indication that the quantities $N_F(\zeta)$ and $(dN_F/dE)_\zeta$ will be as high in Pu as in these other metals. However, we are hesitant about extending the Chandrasekhar-Hulm model so far as to say that it is the major factor involved here. This is because this kind of resistance behaviour is more widespread than we have so far indicated, and because very often the temperature coefficient is almost zero over truly vast ranges of temperature. For instance, Ames and McQuillan (1954) found that the resistance of several β-Ti-Nb alloys scarcely varied at all with temperature over a range of 1200°K to the melting point. It is probable that the low and sometimes negative temperature coefficients in these various metals, including the high temperature phases of Np, U and some transition metals, are related to one another; but no-one has yet given a satisfactory interpretation of this phenomenon. The possibility that spin-disorder effects may be occurring in the appropriate phases of all the metals concerned should certainly receive attention.

5.6. δ-Plutonium Alloys.

The Pu alloys, which were stabilised to the f.c.c. δ-phase by the addition of a few atomic per cent of

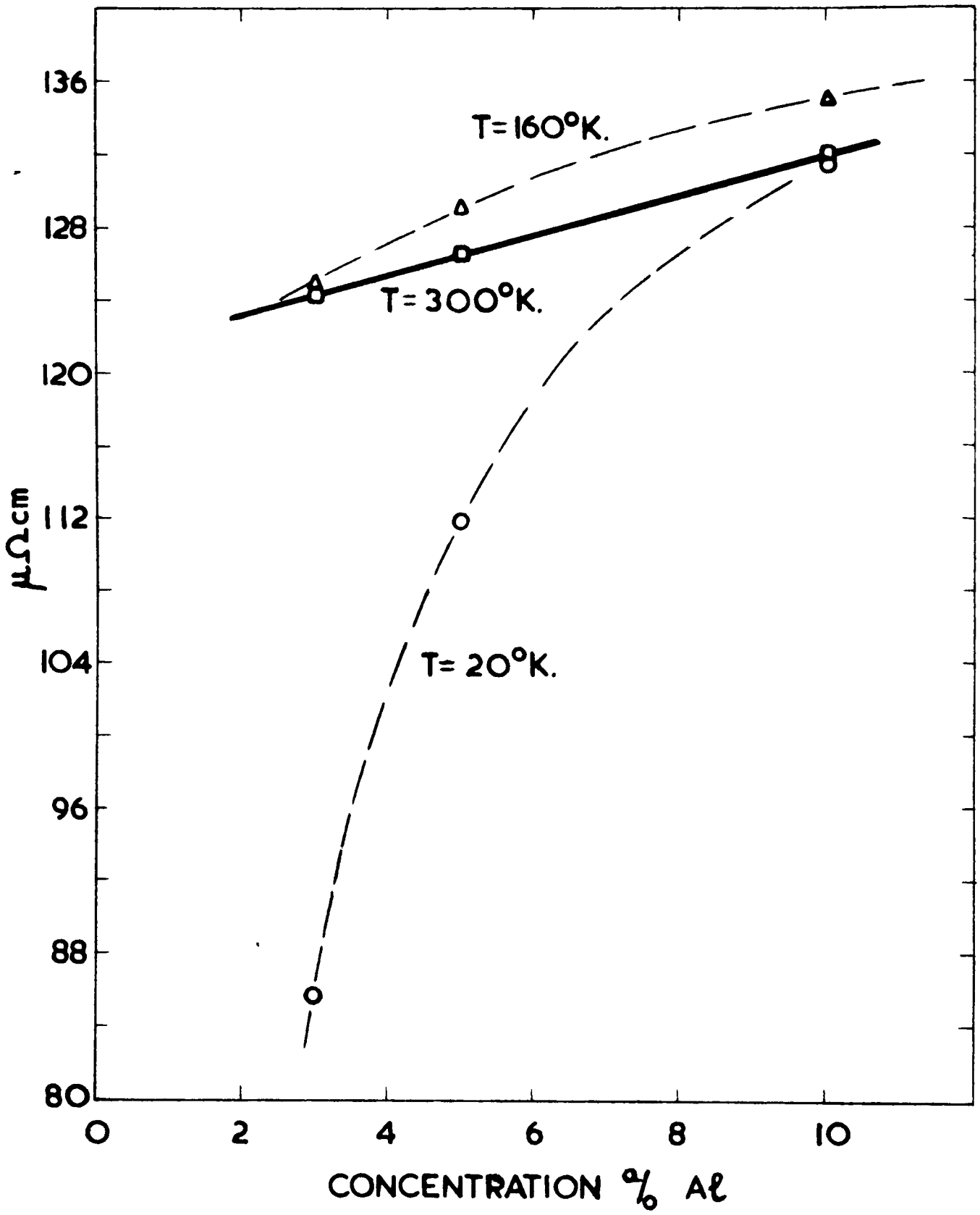

136
128
120
112
104
96
88
80
μΩcm
T=160°K.
T=300°K.
T=20°K.
0
2
4
6
8
10
CONCENTRATION % Aℓ

FIG. 5·9

aluminium, also displayed anomalous resistance behaviour, which was rather similar to that of pure α-Pu (fig. 3.29). This suggests that the same cause may be responsible for the resistance peaks in both phases, and, for reasons already discussed, we feel thatthis is probably due to antiferromagnetism. This would at any rate satisfactorily account for the very rapid increase in resistance (a) upon rise in temperature of the weakest alloy and (b) upon increase in aluminium content measured at $20^{\circ}K$; for increased alloying should inhibit localised spin alignment below the Neel temperature, leading to an abnormally fast rate of increase of resistance with concentration. We would therefore not expect Nordheim's rule of $\rho_{\circ} \propto c(1-c)$ to be obeyed at low temperatures (for $c < 0.2$, $\rho_{\circ} \propto c$), and, as can be seen from fig. 5.9, it does not hold for $T = 20^{\circ}K$. However, at temperatures above the Neel point, where complete spin disorder exists, the contribution to the resistance from this disorder would be constant, and thus roughly equal in all three alloys. A comparison of the resistivity at $160^{\circ}K$ for these alloys shows that here Nordheim's rule is more nearly obeyed.

In fig. 3.29 we see that with increasing aluminium

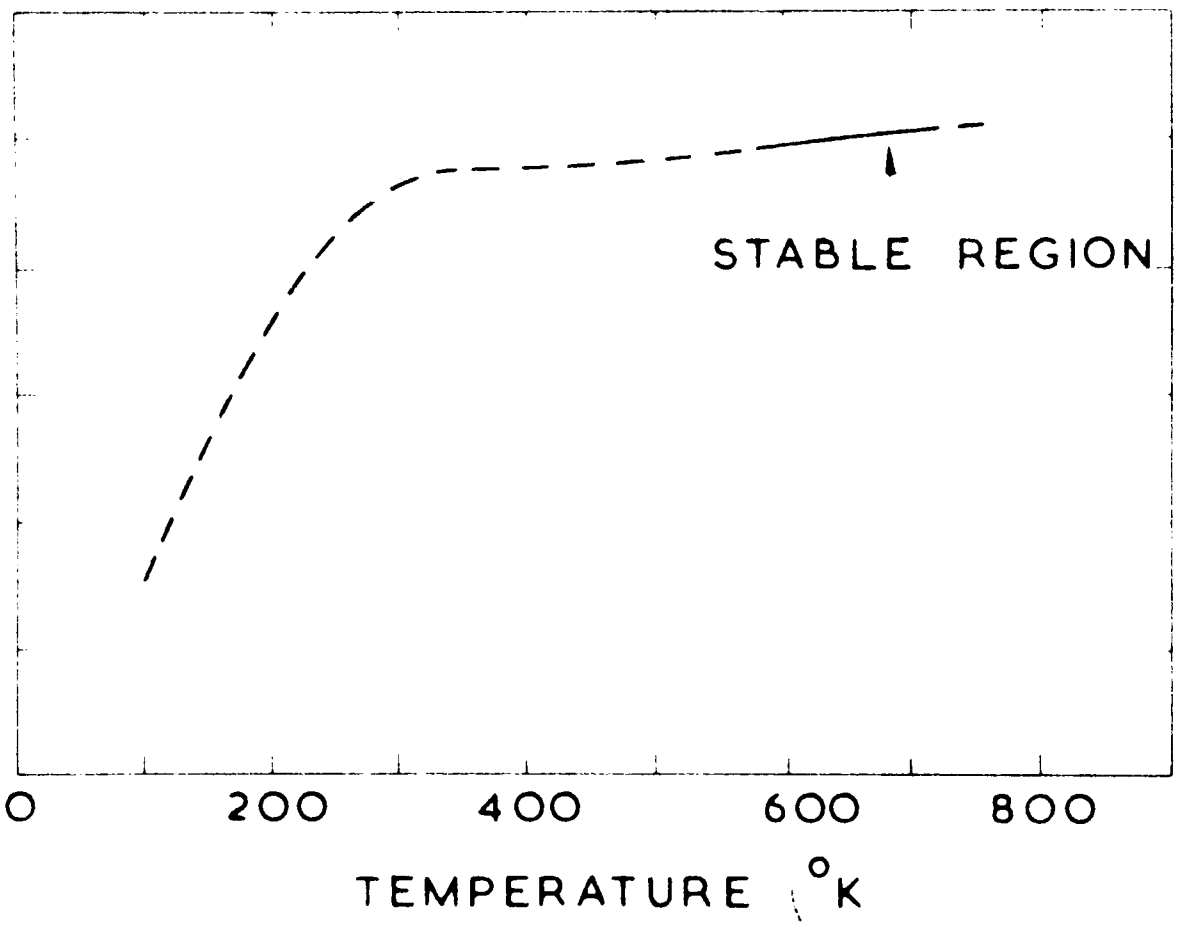


FIG 5 10 SUGGESTED R-T CURVE FOR PURE δ Pu

content the position of ρ_{max} moves towards lower temperatures. Extrapolation to zero aluminium content indicates that in pure δ-Pu ρ_{max} would occur at ~250°K and would roughly equal 115 μΩ cm. This compares with 155 μΩ cm at 105°K in the pure α-phase (the Pu used in the preparation of these alloys was of the same origin as Pu 4). The general features of our curves are qualitatively similar to the manganese rich γ-Mn-Cu alloys studied by Bacon, Dunmur, Smith and Street (1957), and which they showed by neutron diffraction experiments to be antiferromagnetic. There is also a strong resemblance to the titanium rich β-Ti-Mo alloys of Yoshida and Tsuya (1956).

5.6.1. Once again we have in the δ-Pu alloys a series of alloys in which there are negative temperature coefficients over certain ranges of temperature. In the temperature region 590 to 720°K, where ordinary Pu is stable in the δ-phase, the slope is by contrast positive (though small) and fig. 5.10 indicates the form that the complete curve for pure δ-Pu may take. Measurements on these same alloys above room temperature have been performed by King. His curves display shallow minima in the region 500 to 700°K with very low positive slopes at higher temperatures.

The Chandrasekhar-Hulm model can be invoked to give a qualitative explanation of these results too. Chandrasekhar and Hulm explained their own data on γ-U alloys by combining the previously discussed Jones model with the theory of random solid solutions. The contribution to the resistance from the solute atoms ρ_A is a decreasing function of the temperature through its dependence on $N_F(\zeta)$, which involves an equation containing the factor in square brackets in equation (15); whereas the contribution from the lattice vibrations is, as before, an increasing function of the temperature. The relative magnitude of these two terms determines the resulting temperature dependence, and could explain the small temperature coefficients above ρ_{max} in our δ-Pu alloys; but in order to account for the minima it would be necessary to suppose that deviations from the formula for ρ_A occur at higher temperatures. However, since spin-disorder appears responsible for the behaviour at low temperatures (below ρ_{max}), it seems more likely that these small temperature coefficients are related to spin-disordering effects. Neutron diffraction experiments at low temperatures would probably help in elucidating the position.

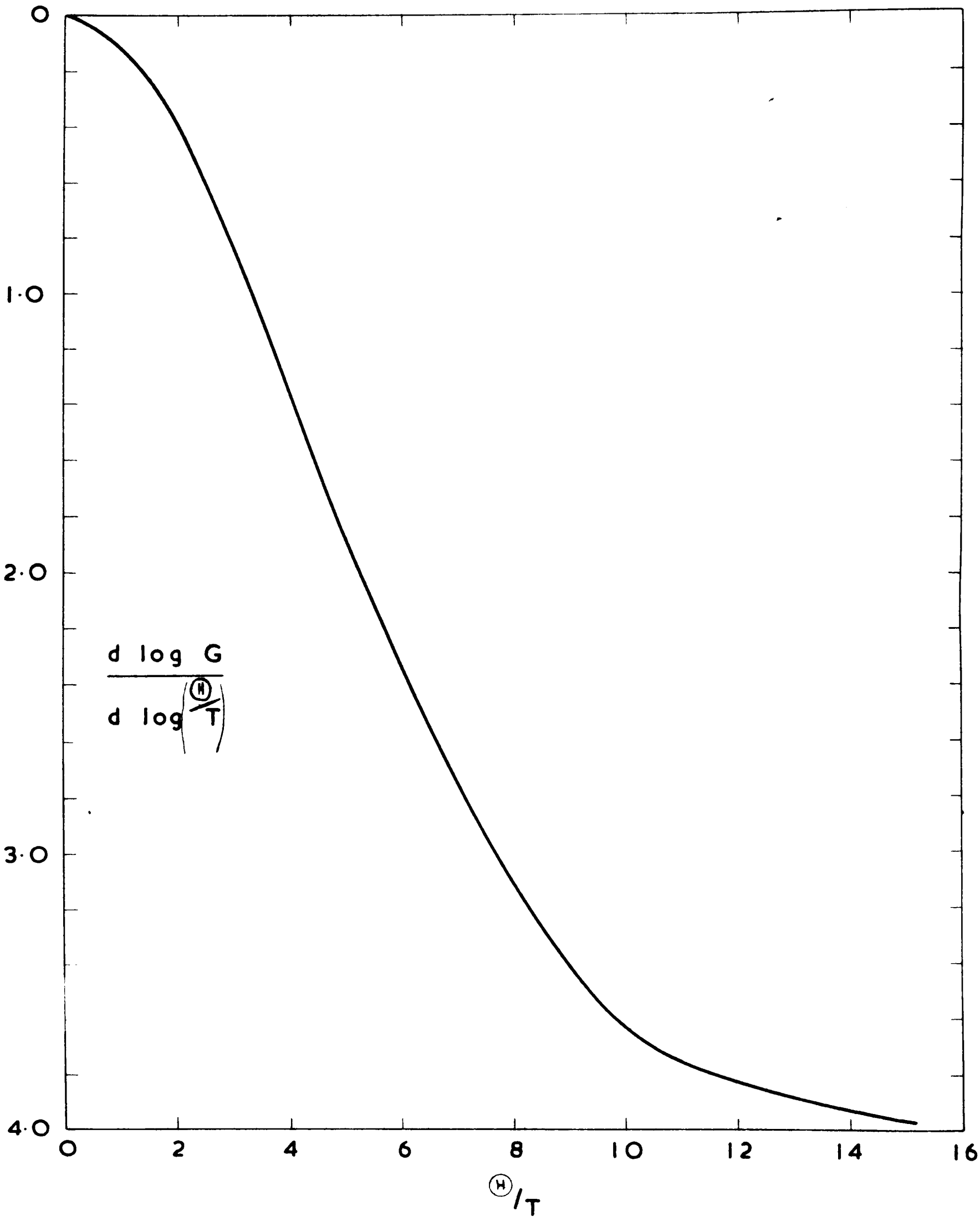
5.7. Concluding Remarks.

The electrical resistances and thermoelectric powers of the four actinide metals dealt with in this thesis have been found to display abnormal temperature relationships, and we have stressed the similarities that these metals have with the rare earth and transition metals, in particular their possession of incompletely filled inner shells. The earlier members of the series appear to be more like the transition metals (especially Th with no 5f electron), but, as we move along the series, we find they become more typically like the rare earths.

Their observed properties seem to justify the description of the band structure in terms of a two-band model, in which one band (the conduction band) is broad with a low density of states and the other band is narrow with a high density of states. The Fermi surface lies in this narrow band, and the magnetic influence of the incomplete 5f and 6d shells is illustrated by the occurrence of ferromagnetism in several alloys and compounds. The resistivity of α- and δ-Pu seems explicable in terms of spin-disorder, and it may be that this occurs amongst the high temperature phases of the other actinides also.

There are several lines along which profitable work can be carried out. For instance, studies should be done on Ac, Pa and Am, which ought to be obtainable in the not too distant future, and on purer Np. Work involving single crystals, especially of Pu, would be valuable, as would work on other Pu isotopes (if ever obtainable). The self-heating of Pu^{242}, for example, is only one tenth that of Pu^{239}, so that its use would make a determination of the low temperature specific heats easier to carry out.

It would also be interesting to see if quenched b.c.c. Np and Pu alloys show the nearly temperature independent resistance at low temperatures that b.c.c. U alloys do. Hall measurements on α- and δ-Pu in the region of ρ_{max} should prove useful too in indicating whether magnetic effects are important. Certainly, low temperature diffraction data on Pu and U should be obtained as a check for possible phase changes, while neutron diffraction studies on α- and δ-Pu, and perhaps γ-U alloys, would be invaluable in resolving doubts concerning spin-disorder effects.


0
1·0
2·0
3·0
4·0
d log G
d log (H/T)
0
2
4
6
8
10
12
14
16
H/T

APPENDIX

TABLE GIVING $\frac{d\log G}{d\log \Theta/T}$ AS A FUNCTION OF $\frac{\Theta}{T}$.

Its use in evaluating Θs from resistance data is explained on p.68. The shape of the function is illustrated in the small scale graph opposite.

Θ/T	$\frac{d\log G}{d\log \Theta/T}$	Θ/T	$\frac{d\log G}{d\log \Theta/T}$	Θ/T	$\frac{d\log G}{d\log \Theta/T}$
		2.6	0.654	6.2	2.446
0.2	0.005$_5$	2.7	0.700	6.4	2.538
0.3	0.0102	2.8	0.747	6.6	2.627
0.4	0.0174	2.9	0.795	6.8	2.707
0.5	0.0271	3.0	0.844	7.0	2.784
0.6	0.0385	3.2	0.893	7.2	2.860
0.7	0.0526	3.3	0.943	7.4	2.932
0.8	0.0710	3.3	0.993	7.6	3.002
0.9	0.0902	3.4	1.044	7.8	3.069
1.0	0.110	3.5	1.095	8.0	3.13
1.1	0.132	3.6	1.146	8.2	3.19
1.2	0.156	3.7	1.197	8.4	3.25
1.3	0.182	3.8	1.249	8.6	3.31
1.4	0.210	3.9	1.301	8.8	3.36
1.5	0.239	4.0	1.354	9.0	3.41
1.6	0.270	4.2	1.461	9.2	3.46
1.7	0.302	4.4	1.568	9.4	3.50$_5$
1.8	0.336	4.6	1.673	9.6	3.55
1.9	0.370	4.8	1.774	9.8	3.59
2.0	0.405	5.0	1.873	10.0	3.63
2.1	0.442	5.2	1.970	11.0	3.75
2.2	0.481	5.4	2.066	12.0	3.83
2.3	0.522	5.6	2.162	13.0	3.88$_5$
2.4	0.565	5.8	2.257	14.0	3.93
2.5	0.609	6.0	2.352	15.0	3.96$_5$

References.

Adams, L.H. (1926): International Critical Tables, p.57.

Ahlberg, J.E. and Lundberg, W.O. (1935): J.Am.Chem.Soc.57,2722

Alekseyevsky, N.E. and Migunov, L. (1947):J.Phys.USSR.11, 95.

Ames, S.L. and McQuillan, A.D. (1954): Acta Met. 2, 831.

Aschermann, G. and Justi, E. (1942): Phys.Z. 13, 207.

Aston, J.G., Willinghanz, E. and Messerley, G.H. (1935):
J.Am.Chem.Soc. 57, 1642.

Baber, W.G. (1937): Proc.Roy.Soc. A 158, 383.

Bacon, G.E., Dunmur, I.W., Smith, J.H. and Street, R. (1958):
Proc.Roy.Soc. 241, 223.

Bailyn, M. (1958): Phys.Rev. 112, 1587.

Bailyn, M. and Brooks, H. (1956): Bull.Am.Phys.Soc. 1, 300.

Bardeen, J. (1937): Phys.Rev. 52, 688.

Barrett, C.S. (1956): Acta Cryst. 9, 671.

Bates, L.F. and Mallard, J.R. (1950): Proc.Phys.Soc. 63B, 530

Bender, D. (1949): Zeits.f.Metallkunde 40, 257.

van den Berg, M. and Klinkenberg, P.F.A. (1954): Physica 20,461

Berlincourt, T.G. (1959): Phys.Rev. 114, 969.

Bijl, D. and Pullan, H. (quoted in Rosenberg, 1955).

Blackman, M. (1951): Proc.Phys.Soc. 64A, 681.

la Blanchetais, C.H. and Trombe, M.F. (1956): Compt.Rend.
243, 707.

Blatt, F.J. (1961): J.Phys.Chem.Solids 17, 177.

Bloch, F. (1928): Zeits.F.Phys. 52, 555.

Bloch, F. (1929): Zeits.f.Phys. 53, 216.

Bodine, J.H. (1956): Phys.Rev. 102, 1459.

Borelius, G., Keesom, W.H., Johansson, C.H. and Linde, J.O. (1930): Proc.Acad.Sci.Amst. 33, 17 (Leid.Comm. 206a).

do. (1931): Proc.Acad.Sci.Amst. 34, 1365 (Leid.Comm. 217c).

do. (1932): Proc.Acad.Sci.Amst. 35, 10 (Leid.Comm.Suppl. 70a).

Bridge, J.R., Schwartz, C.M. and Vaughan, D.A. (1956): J.Metals 8, 1282.

Chandrasekhar, B.S. and Hulm, J.K. (1958): J.Phys.Chem. Solids 7, 259.

Christian, J.W., Jan, J.P., Pearson, W.B. and Templeton, I.M. (1958): Proc.Roy.Soc. A 245, 213.

Clement, J.R. and Quinnell, E.H. (1952): Rev.Sci.Instr. 23, 213

Coles, B.R. (1958): Adv.Phys. 7, 40.

Colvin, R.V., Legvold, S. and Spedding, F.H. (1960): Phys. Rev. 120, 742.

Corliss, L.M., Hastings, J.M. and Weiss, R.J. (1959): Phys. Rev.Letters 3, 211.

Costa, P. (1960): J.Nucl.Materials 2, 75.

Curry, M.A., Legvold, S. and Spedding, F.H. (1960): Phys. Rev. 117, 953.

Dahl, A.I. and van Dusen, M.S. (1947): J.Res.N.B.S. 39, 53.

Dawson, J.K. (1954): J.Chem.Soc. 5329, 3393.

Dean, D.J., Kay, A.E. and Loasby, R.G. (1958): J.Inst. Metals 86, 464.

van Dijk, H., Durieux, M., Clement, J.R. and Logan, J.E. (1958): Physica 24, S 129.

Drude, P. (1900): Ann.der Phys. 1, 566.

Evans, J.P. and Mardon, P.G. (1959): J.Phys.Chem.Solids 10, 311

Friedel, J. (1956): J.Phys.Chem.Solids 1, 175.

Giauque, W.F., Buffington, R.M. and Schulze, W.A. (1927a): J.Am.Chem.Soc. 49, 2343.

Giauque, W.F., Johnston, H.L. and Kelley, K.K. (1927b): J.Am.Chem.Soc. 49, 2367.

Ginnings, D.C. and Corruccini, (1947): J.Res.N.B.S. 39, 309.

Gold, A.V., MacDonald, D.K.C., Pearson, W.B. and Templeton, I.M. (1960): Phil.Mag. 5, 765.

Goodman, C.B. and Shoenberg, D. (1950): Nature 165, 441.

Griffel, M. and Skochdopole, R.E. (1953): J.Am.Chem.Soc.75, 5250

Grube, G. and Speidal, H. (1940): Z.Elektrochem. 46, 233.

Gruneisen, E. (1933): Ann.der Phys. 16, 530.

Gurevich, L. (1945): J.Phys.Moscow 9, 477.

Gurevich, L. (1946): J.Phys.Moscow 10, 67.

Hall, P.M., Legvold, S. and Spedding, F.H. (1960): Phys. Rev. 117, 971.

Hein, R.A., Henry, W.E. and Wolcott, N.M.(1957): Phys.Rev. 107, 1517.

Hill, J.D. (1959): J.Sci.Instr. 36, 369.

Houston, W.V. (1928): Zeits.f.Phys. 48, 449.

James, N.R., Legvold, S. and Spedding, F.H. (1952): Phys. Rev. 88, 1092.

Jan, J.P., Pearson, W.M. and Templeton, I.M. (1955): Can.J.Phys. 36, 627.

Jones, H. (1956): Handbuch der Physik 19, 227.

Jones, W.M., Gordon, J. and Long, E.A. (1952): J.Chem. Phys. 20, 695.

Kelly, F.M. and MacDonald, D.K.C. (1953): Can.J.Phys. 31, 147

Kiess, C.C., Humphreys, C.J. and Laun, D.D. (1946): J.Res. N.B.S. 37, 57.

Kilpatrick, J.E., Hammel, E.F. and Mapother, D. (1955): Phys.Rev. 97, 1634.

Lee, J.A., Evans, J.P., Hall, R.O.A.H. and King, E. (1959): J.Phys.Chem.Solids 11, 278.

Lee, J.A., Mardon, P.G., Pearce, J.H. and Hall, R.O.A.H. (1959): J.Phys.Chem.Solids 11, 177.

Lee, J.A., Meaden, G.T., Hall, R.O.A.H. and King, E. (1960); Memoire 4, Conf.Int.Met.Plutonium, Grenoble.

Lee, J.A., Meaden, G.T. and Mendelssohn, K. (1959): Proc. Phys.Soc. 74, 671.

do. (1960): Cryogenics 1, 52.

Lehman, G.W. (1956): U.S.A.E.C. Report NAA-SR-1659

Lehman, G.W. (1957): U.S.A.E.C. Report NAA-SR-1839

Liddiard, A.B. (1954): Proc.Roy.Soc. A 224, 161.

Lomer, W.M. and Ridley, E.C. (1958): ISMET 1958 BP 337

Lord, W.B.H. and Waldron, M.B. (1957): J.Inst.Metals 86, 385.

Lorentz, H.A. (1905): Proc.Acad.Sci.Amst. 7. 438, 585.

Lounasmaa, O.V. (1958): Phil.Mag. 3, 652.

MacDonald, D.K.C. (1956): Handbuch der Physik 14, 137.

MacDonald, D.K.C. and Mendelssohn, K. (1950): Proc.Roy. Soc. A 202, 103.

Meaden, G.T. and Lee, J.A. (1960): Cryogenics 1, 33.

Meechan, C.J. (1955): At.Int.Q.Pr.Rep.: Sol.St.Phys., p.20

Meissner, W. (1929): Naturwiss. 17, 390.

Meissner, W. and Voigt, B. (1930); Ann.der Phys. 7, 892.

Middleton, A.E. and Scanlon, W.W. (1953): Phys.Rev. 92, 819.

Mott, N.F. (1936): Proc.Roy.Soc. A 153, 699.

Mott, N.F. and Jones, H. (1936): Theory of Properties of Metals and Alloys.

Nairn, J.S., Collins, D.A., McKay, H.A.C. and Maddock,A.G. (1958): Proc.I.C.P.U.A.E., Geneva 17, 216.

North, J.M. (1952): A.E.R.E. M/R 1016.

Pearson, W.B. And Templeton, I.M. (1955): Proc.Roy.Soc. A 231,534

Peierls, R. (1932): Ann.der Phys. 12, 154.

Potter, H.H. (1941): Proc.Phys.Soc. 53, 695.

Powell, R.L., Bunch, M.D. and Corruccini, R.J. (1961): Cryogenics 1, 139.

Ridley, E.C. (1958): Proc.Roy.Soc. A 247, 199.

Rosenberg, H.M. (1955): Phil.Trans.Roy.Soc.Lond. A 247, 441.

Sandenaw, T.A. (1960): Mem. 43, Conf.Int.Met.Pu, Grenoble.

Sandenaw, T.A. and Gibney, R.B. (1958): J.Phys.Chem.Solids 6, 81

Sandenaw, T.A. and Olsen, C.E. (1960): Memoire 41, Conf. Int.Met.Plutonium, Grenoble.

Sandenaw, T.A., Olsen, C.E. and Gibney,R.B. (1960): Memoire 42, Conf.Int.Met.Plutonium, Grenoble.

Schuch, A.F. and Laquer, H.L. (1952): Phys.Rev. 86, 803.

Scott, R.B. (1941): p.212 in Temperature, Its Measurement and Control in Science and Industry.

Shoenberg, D. (1940): Proc.Camb.Phil.Soc. 36, 84.

Shoenberg, D. (1952): Superconductivity, C.U.P.

Shomate, C.H.(1945): J.Chem.Phys. 13, 326.

Shull, C.G. and Wilkinson, M.K. (1953):Rev.Mod.Phys. 25, 100.

Smith, P.L. and Wolcott, N.M. (1955): Conf.Phys.Basses Temps, Paris (p.103 Suppl.Bull.Inst.Int.Froid).

Sommerfeld, A. (1928): Zeits.f.Phys. 47, 1.

Southard, J.C. and Andrews, D.H. (1929): J.Franklin Inst.207,323

Southard, J.C. and Milner, R.T. (1933): J.Am.Chem.Soc.55, 4384

Stout, J.W. and Jones, W.M. (1947): Phys.Rev. 71, 582.

Thompson, J.G. (1933): Metals and Alloys, 4, 114.

Tredgold, R.H. (1954): Proc.Phys.Soc. 67A, 1018.

Tyler, W.W., Wilson, A.C. and Wolga, G.J. (1953): J.Metals 5, 1838

Wallace, D.C. (1960): Phys.Rev. 120, 84.

Walton, G.N. (1958): (Ed.) Glove-Boxes and Shielded Cells for Handling Radioactive Materials.

Weil, L., Quezel, G., Cohen, J. and Pascard, R. (1960): Conf.Int.Met.Plutonium, Grenoble.

Weiner, Chiotti, P. and Wilhelm, H.A. (1952): U.S.A.E.C. Publ. (ISC-305).

White, G.K. and Woods, S.B. (1957): Can.J.Phys. 35, 346.

White, G.K. and Woods, S.B. (1959): Phil.Trans.Roy.Soc. Lond. A 251, 273.

Wilson, A.H. (1938): Proc.Roy.Soc. A 167, 580.

Wilson, A.H. (1953): The Theory of Metals. C.U.P.

Wolcott, N.M. and Hein, R.A. (1958): Phil.Mag 3, 591.

Yoshida, S. and Tsuya, Y. (1956): J.Phys.Soc.Japan 11, 1206.

Ziman, J.M. (1954): Proc.Roy.Soc. A 226, 436.

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