

Low temperature resistance anomalies in alloys
and an application in thermometry

A thesis submitted for the degree of
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by

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ABSTRACT

This thesis reports measurements which have been made of the electrical resistivities of some alloys of transition metals at low temperatures. The alloys fall into two groups. The first are rhodium based alloys, containing less than 1% of 3 d solute, and the second are alloys in which a small quantity of a transition element (usually iron) is dissolved in vanadium or a binary alloy of vanadium and chromium.

The resistivity of Rh Fe had already been measured down to 0.4 K but theoretical predictions for its behaviour made it desirable to take the measurements to lower temperatures. Using a dilution refrigerator, such measurements have been accomplished down to 0.02 K, and the concentration dependence of the resistivity has been investigated. The resistivities of rhodium alloys with Cr, Mn and Co solutes are also reported.

The resistivity of rhodium-iron had by its large monotonic temperature dependence suggested itself as a resistance thermometer particularly at low temperatures where platinum thermometry is impracticable. The rhodium-iron thermometer has been developed in this project and its performance and viability are discussed in chapter 4.

The resistance anomalies due to the presence of iron in chromium-rich vanadium-chromium alloys were found to have a negative temperature coefficient and low temperature 'Kondo' minima were observed. The form and magnitude of the effects in various (V-Cr) Fe compositions were investigated and in spite of the difference in the sign of the temperature dependence, certain similarities with the resistivity of Rh Fe were found.

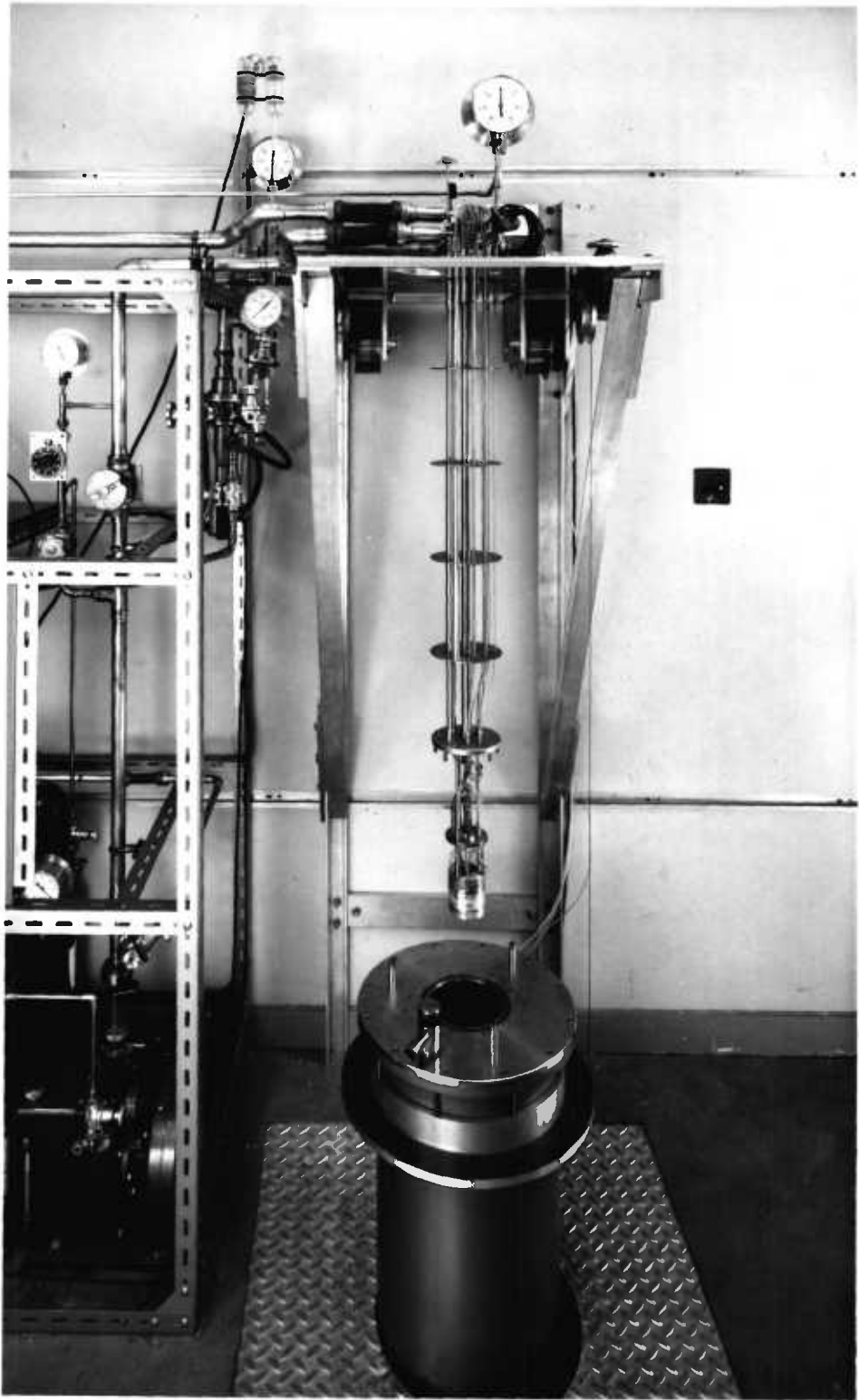


Plate 1. ^3He Cryostat: general view

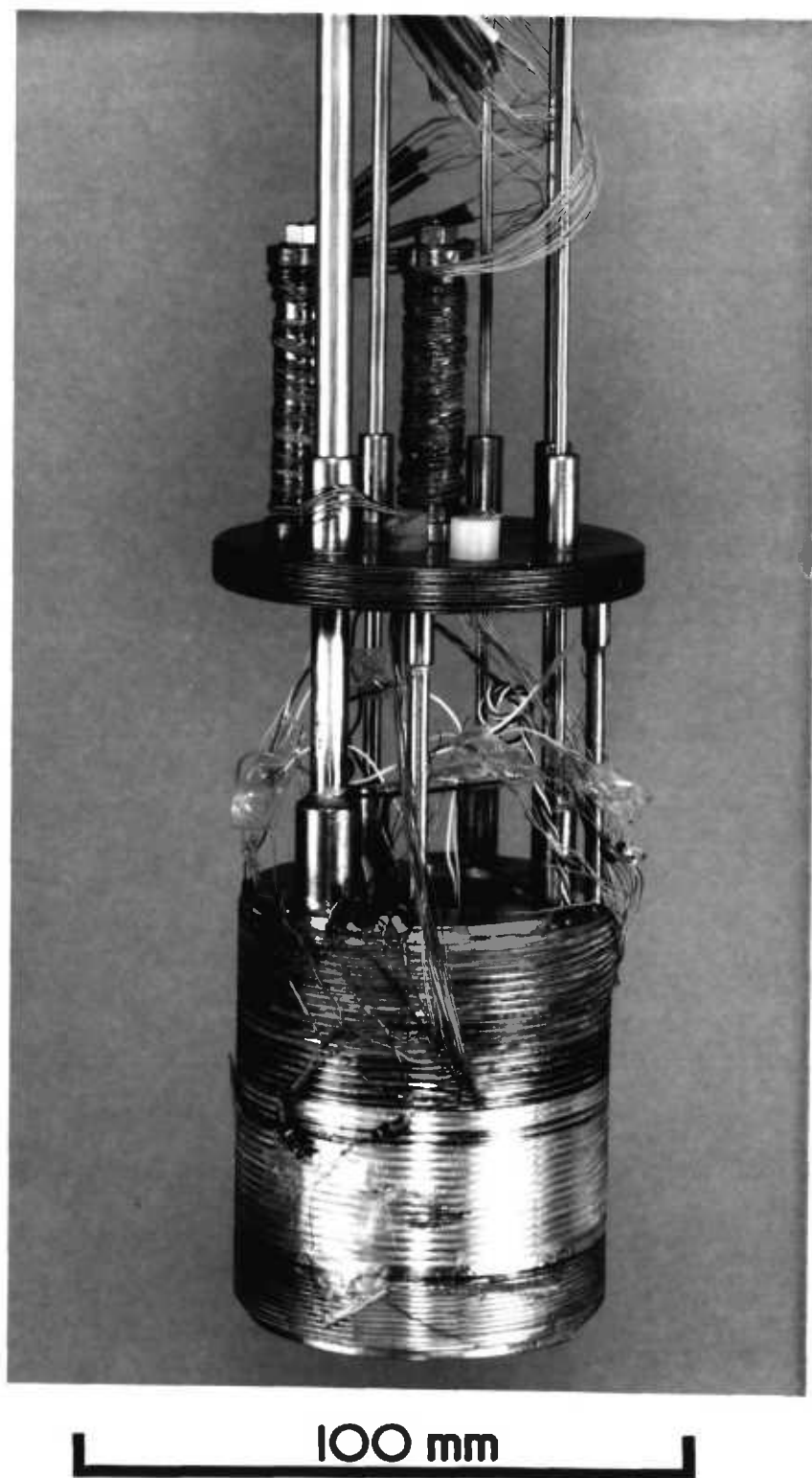


Plate 2. ^3He Cryostat: view of the thermometer block, containing germanium thermometers.

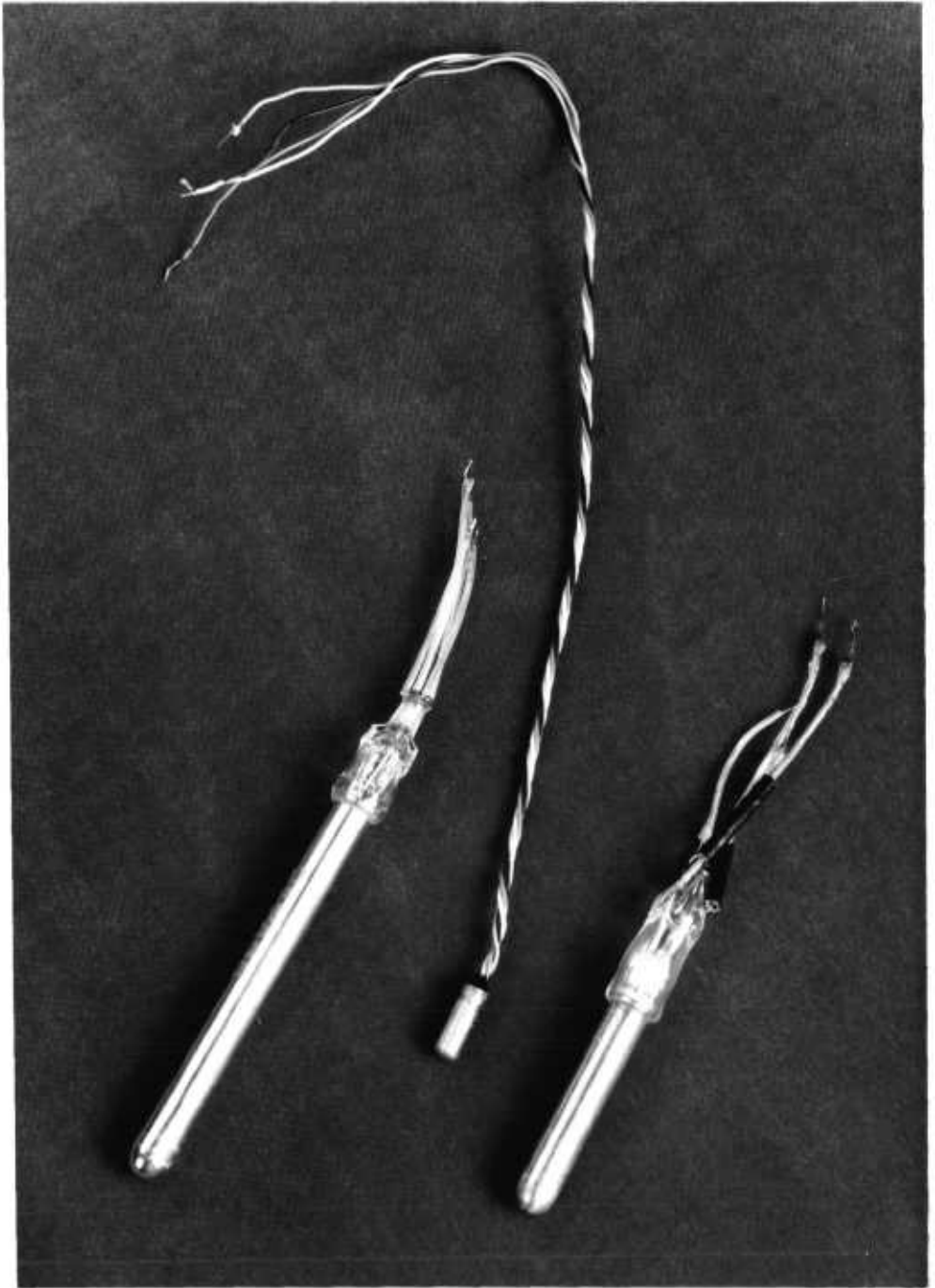


Plate 3. Low temperature resistance thermometers, approximately life size: left to right, platinum, germanium, rhodium-iron.

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I would also like to record my appreciation of the assistance of Engelhard Industries Ltd in the preparation of the rhodium-iron wire, and H Tinsley and Co Ltd in the construction of the thermometers.

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INTRODUCTION

A high electrical conductivity is the sine qua non of a metal, and the physics of metals and alloys is naturally to a great extent concerned with their electronic properties. The transport properties, including the electrical conductivity, follow from a solution of the Boltzmann equation in which the net rate of gain of momentum of the electronic system from electric and magnetic fields and thermal activation is balanced by the net loss due to collisions with, for example, the vibrating lattice. On the assumption that a relaxation time characterises each collision process, general expressions for the transport coefficients may be derived. Experimental determinations of these quantities lead to a knowledge of the relaxation times for each scattering process, which in turn give information concerning the interactions involved in the collisions. In this thesis the electrical conductivity has been used to obtain information on the way in which transition element impurity atoms scatter the conduction electrons of a metallic host, and on how the magnitude of the resulting resistivity^{*} is dependent on the temperature. The field is not new: the resistivity anomalies in dilute alloys containing a small quantity of transition elements (in particular the resistance minimum behaviour) were first observed in noble metal hosts in the 1930s. It was not until 1964, however, when Sarachik et al. demonstrated the link between the presence of a localised magnetic moment on the impurity and the observation of a resistance minimum in (Nb - Mo) Fe alloys, that Kondo propounded his

* As resistivities due to different scattering mechanisms tend to be additive - Matthiessen's rule - it is more convenient to discuss the resistivity than its inverse, the conductivity.

theory showing how the two could be connected. In the same year the discovery by Coles that the anomaly in Rh Fe was markedly different from the resistivity minimum of the 'Kondo Effect', showed that the theory was still incomplete, and it was only in 1972 that a single theory capable of application to both 'Kondo alloys' and 'Coles alloys' was developed, based on the concept of localised spin fluctuations (Rivier and Zlatic 1972 a and b).

The remarkable feature of the resistivity of dilute rhodium-iron is that it shows a very large reduction as the temperature falls below about 30 K and that the slope $d\rho/dT$ continues to increase at least down to about 1 K. Thus Coles was able to conclude his original paper with the suggestion that 'it seems likely that these materials could form very useful resistance thermometers down to very low temperatures'. The possibility has been extensively investigated in this project and such a thermometer, though not without its disadvantages, would indeed seem to have some important applications.

The nature of the resistivities of alloys of rhodium with iron and some other 3d solutes has also been investigated. Some interesting concentration dependences were discovered in Rh Fe, and by using the NPL dilution refrigerator the predicted T^2 dependence of the resistivity below 1 K was sought and found. The resistivities of ternary alloys of (V - Cr) Fe were also measured as the nature of an anomaly which might be observed could not easily be predicted. In the event no anomalies were found in the vanadium-rich alloys but resistance minima were found in some chromium-rich alloys. Here again the dependence of the anomaly on the iron concentration was investigated and a strong parallelism was found between this and the Rh-Fe system which lends support to the Rivier-Zlatic universal theory of spin fluctuations.

The outline of the thesis is clear from the contents list. After a review of some relevant theoretical and experimental work (Chapter 1)

a description of the apparatus and the experimental methods is given in Chapter 2. Then in Chapter 3 the results of the measurements of the resistivities of the rhodium based alloys are presented and a description of the development of the rhodium-iron thermometer follows in Chapter 4. Finally the resistivity measurements of V-Cr alloys are described in Chapter 5.

The convention of underlining certain components of an alloy system, such as Rh Fe or (V-Cr) Fe, indicates that iron is present as an impurity in Rh or V-Cr hosts. The references are given at the end of the thesis in alphabetical order of author's name, and this is also used as an author index to the thesis.

CHAPTER 1

REVIEW OF THEORY AND EXPERIMENT

1.1 Conductivity in metals

In the classical theory of electrical conduction in metals, the electrons are accelerated by the electric field F and are scattered by collisions with atoms. They achieve a mean drift velocity v given by

$$v = eF \tau / m$$

where τ is the mean time between collisions and m and e are the electronic mass and charge. Since the current density $j = nev$, where n is the number of conduction (or valence) electrons per unit volume, the conductivity σ is derived:-

$$\sigma = j/F = ne^2 \tau / m \quad \dots (1)$$

Although the classical interpretation of this formula was incorrect and the agreement between theory and experiment obtained in some cases was fortuitous, the concept of the collision (or relaxation) time is valid in modern theory and equation (1) is still appropriate, modified by replacing m by the 'effective' mass m^* , or n by the 'effective' number of electrons, n_{eff} .

With the advent of the quantum theory it became apparent that the electrons, which are now Bloch waves with the periodicity of the lattice, are able to travel freely through a crystal, and are only scattered by lattice imperfections. The mean free path may therefore be long. Furthermore, in order to accommodate all the electrons in distinct states as required by the Pauli principle, occupied states must extend up to a high energy, the Fermi energy, E_F . Electrons whose energy lie more than $\sim k_B T$ below E_F (k_B is the Boltzmann constant) are unable to undergo scattering, there being no unoccupied final state available. As the degeneracy

temperature T_F given by $k_B T_F = E_F$ is $\sim 10^4$ K, the thermal blurring of the Fermi level is small at ordinary temperatures and the distribution function f_0 giving the probability of occupation of an electron state falls rapidly from 1 to 0 as the energy passes through E_F .

At equilibrium this Fermi distribution is symmetrical with respect to the sign of k , the electron wave vector, ie $f_0(k) = f_0(-k)$ and there is no net flow of charge. In an applied field the electrons are accelerated and the Fermi distribution is shifted in the direction of the field, say the x direction, so that at time t

$$f(k) = f_0\left(k_x - \frac{eFt}{\hbar}, k_y, k_z\right).$$

However $f(k)$ is also changed as a result of scattering which tends to restore the distribution to equilibrium; that is, the electrons tend to lose momentum on collision. In the steady state the rate of change of $f(k)$ due to these causes must add to zero, thus:-

$$\frac{df(k)}{dt} = -\frac{eF}{\hbar} \frac{df_0(k)}{dk_x} - \frac{f(k) - f_0(k)}{\tau(k)} = 0$$

where for generality the relaxation time is allowed to be k dependent.

The current density j is given by

$$j = \int_{k \text{ space}} en \left[f(k) - f_0(k) \right] v dk$$

where n is the number of electrons in volume element dk of k space and v is the group velocity of the Bloch waves

$$v = \frac{d\mathcal{P}}{d(1/\lambda)} = \frac{1}{\hbar} \frac{dE}{dk}$$

Therefore

$$\sigma = j/F = - \int_{k \text{ space}} n \frac{e^2}{\hbar^2} \tau(k) \frac{df_o(k)}{dk_x} \frac{dE}{dk} dk \quad \dots (2)$$

This is the general expression for the conductivity σ in a single Brillouin zone which is in principle solved if the band structure and relaxation time are known. Since $(df_o(k)/dk_x)$ is zero except within $\sim k_B T$ of E_F it may be seen that σ depends only on the value of the expression near the Fermi level. Integrating eq 2 by parts gives

$$\sigma = - \left[\frac{n e^2}{\hbar^2} \tau(k) \frac{dE}{dk} f_o(k) \right]_0^\infty + \int_0^\infty \frac{n e^2}{\hbar^2} \frac{\partial}{\partial k_x} \left(\tau(k) \frac{dE}{dk} \right) f_o(k) dk$$

The first term is zero at both limits while the second may be replaced by an average provided that $\tau(k) \frac{dE}{dk}$ does not vary rapidly near E_F

Thus

$$\sigma = \frac{n e^2}{\hbar^2} \left[\frac{\partial}{\partial k_x} \left(\tau(k) \frac{dE}{dk} \right) \right]_{E_F} \quad \dots (3)$$

For free electrons $\tau(k) \rightarrow \tau$ and $E = \hbar^2 k^2 / 2m$ and the classical expression (1) is recovered. It is convenient in real cases to define either an effective mass m^* or an effective number of electrons n_{eff} from equation (3) so that the simple form of (1) may still be employed.

In spite of its evident importance in determining σ , for a given metal or alloy n_{eff} or m^* may usually be considered independent of temperature. Resistivity measurements may give useful information on n_{eff} as an alloy composition is varied, but this work is primarily concerned with resistivity as a function of temperature. By far the more important parameter is the

relaxation time and the experiments are aimed at determining the nature of the scattering mechanisms and the interactions which cause them.

1.2 Resistivity as a function of temperature in pure metals

The temperature dependence of the scattering of conduction electrons by lattice vibrations is discussed at length in many texts (eg Mott and Jones 1936, Ziman 1960). At temperatures greater than the Debye temperature Θ_D the phonon wavelengths are shorter than the interatomic distance and the atoms may be considered to be displaced at random. The resistivity is then proportional to the mean square displacement which in turn is proportional to T/Θ_D^2 . At low temperatures ($T < 0.1 \Theta_D$) the quantisation of lattice vibrations must be taken into account. The scattering probability depends on the density of phonons, which is proportional to T^3 , and is constrained by the laws of conservation of momentum and energy. Furthermore, the phonon wave-number is small at low temperatures so that the change in electron momentum on collision is small. These factors together give a resistivity proportional to T^5/Θ_D^6 . The high and low temperature regimes are combined in the Bloch-Gruneisen law which covers the whole range and has some experimental justification particularly for monovalent metals. In divalent and transition metals where the band structure is more complicated, departures from the law may be expected. Furthermore, other scattering mechanisms such as electron-electron collisions add to the 'ideal' resistivity and may in some metals provide the dominant contribution over part of the temperature range.

Transition elements are differentiated from other elements by the presence of an unfilled d shell. The spatial extent of the d electrons in the atom is small compared with that of the s electrons and correspondingly in a metal the overlap of the d wave functions of neighbouring atoms is relatively small. The s electrons provide

the cohesion, their wavefunctions extending over the whole crystal, while the d states are only broadened into a narrow band, which in order to accommodate 10 electrons per atom must have a high density of states. That the d band does exist and contributes to the Fermi surface is evidenced by the high electronic specific heat of the transition metals, and it has far-reaching consequences in their magnetic and electrical properties.

A theory for the electrical resistivity of transition metals was developed by Mott (1935, 1936 a and b) on the assumption that the narrow d band is situated in energy within the broad s band, as shown schematically in fig 1.1. The Fermi level intersects both bands such that the total number of occupied states is equivalent to the appropriate number of electrons per atom. Transitions from one

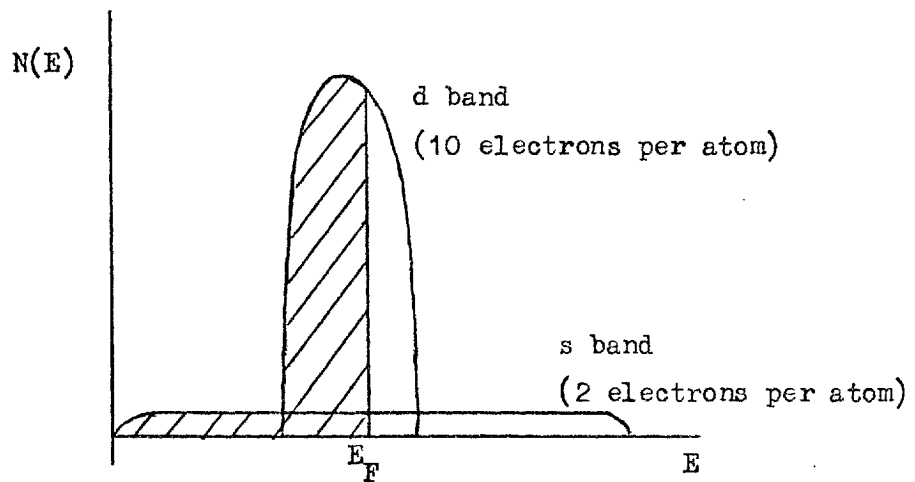


Fig 1.1. Schematic density of states curve for a transition metal.

band to the other as a result of scattering may occur and their probability is dependent on the density of states at E_F in each band. Thus assuming s and d electrons scatter independently, the relaxation

times may be written:-

$$\frac{1}{\tau_s} \propto |U_{sd}|^2 N_d(E_F) + |U_{ss}|^2 N_s(E_F)$$

and

$$\frac{1}{\tau_d} \propto |U_{dd}|^2 N_d(E_F) + |U_{sd}|^2 N_s(E_F)$$

where for example U_{sd} is the scattering potential for a transition from an s to a d state and $N_s(E_F)$ and $N_d(E_F)$ are the s and d densities of states at E_F . If the magnitudes of the potentials are not too different, the first term in each expression dominates, since $N_d(E_F) \gg N_s(E_F)$. In spite of this, the d electrons make only a small contribution to the current because they are relatively localised and have low mobility. The s electrons are as free to conduct as they are in a noble metal, but the large probability of scattering into a d state gives rise to a large resistivity. The plausibility of this model has been demonstrated by experiments on Pd Ag alloys. The resistivity of palladium at 0 °C is about 7 times that of silver. As silver is added to palladium the change in resistivity between 4.2 K and 293 K shows a large reduction which continues until 65% silver is added (Coles and Taylor 1962). The electronic specific heat, a measure of the density of states, shows a similar reduction at least up to 60% silver, which clearly suggests that at this point the d band is filled (Hoare and Yates 1957) and that it is the cause of the high resistivity in palladium.

The Bloch-Gruneisen law is in principle unaffected by the introduction of the d band, though the s - d scattering model is able to explain some departures which are observed at high temperatures (apart from the thermal expansion effect which causes a decrease in θ_D and an increase in the resistivity above the linear law). The density

of states (and therefore γ_s) in transition metals varies rapidly with energy particularly near the top of the band (eg in Pd and Pt). In solving equation 2 it was assumed that γ could be considered constant in the narrow range $\sim k_B T$ from the Fermi level. In Pd and Pt at high temperatures this is no longer justified; s electrons of high energy are scattered less frequently than those at E_F and the resistivity falls below the Gruneisen law. Mott (1936a, Jones 1956) deduced that the law should be multiplied by a factor $(1 - AT^2)$ where A is a function involving the first and second derivatives of $N(E)$ with respect to energy, evaluated at E_F . Assuming that the top of the d band is parabolic he calculated reasonable values for A to account for the effects in Pd and Pt. He also suggested that the complicated shape of the d band could give negative values of A in certain cases, and could therefore account qualitatively for the anomalous resistivity increase observed in Wolfram.

In addition to the large resistivity due to phonon scattering, transition metals may also derive a significant resistivity from electron-electron collisions. These may contribute in any situation in which the Fermi surface is not spherical, but are particularly important where both holes and electrons are present since under an applied field these travel in opposite directions. The resulting collisions can give scattering through large angles and hence a large resistivity. The first treatment of this effect is due to Baber (1937) who found that the resistivity is proportional to T^2 . Qualitatively this is because an electron may only be scattered by a second electron which lies within $k_B T$ of E_F and its final state is also limited to $\pm k_B T$ of E_F . At a sufficiently low temperature the resulting T^2 resistivity gives a larger contribution than the T^5 phonon scattering term. It is not expected to be observed in monovalent metals even at 1 K but in the transition metals Nb, W, Fe, Co, Ni, Pd, Pt, White

and Woods (1959) were able to show that the resistivities tend towards a T^2 dependence below 10 K.

Although Baber scattering may well contribute a significant term to the low temperature resistivity in some of these cases, it seems likely that magnetic effects make a more important contribution, particularly in the ferromagnetic metals Fe, Co and Ni. In these the scattering of conduction electrons by spin waves (magnons) is expected to produce a resistivity proportional to T^2 and the Mills and Lederer (1966) theory of the resistivity of palladium, which is nearly ferromagnetic, also leads to a T^2 dependence. Neither of these effects can be distinguished experimentally from the Baber effect and their relative importance in each metal is therefore uncertain. As the resistivities of the ferromagnetic metals show large variations near the Curie points, however, it would seem that in these the Baber scattering is relatively unimportant. Mott was able to extend his theory to account for the resistivity of nickel as follows. Above the Curie point the spin of a d electron is equally probably in either direction and the resistivity is similar to that of palladium. Below the Curie point spontaneous magnetisation of the d band occurs until at low temperatures the d band of, say, spin + is filled. During this magnetisation the density of spin + d states is continually falling and the probability for phonon induced $s \rightarrow d$ transitions for spin + s electrons is reduced. The resistivity of nickel therefore falls below what would be expected in the absence of ferromagnetism and exhibits a distinct change of slope at the Curie point T_c . This model is evidently inapplicable to rare earth ferromagnetics such as gadolinium in which the f electrons do not form a band. In this case the resistivity above T_c contains a large term due to the scattering of conduction electrons from disordered localised spins which is approximately independent of temperature, while below

T_c the resistivity falls roughly linearly with temperature as order prevails. In iron neither model is wholly satisfactory. While the d band certainly exists, the spontaneous magnetisation is incomplete even at the absolute zero and the Mott theory is not obviously applicable. Experimental results indicate the presence of a large temperature independent resistivity above T_c , due to spin disorder, but that below T_c the resistivity seems more akin to that of nickel than gadolinium (Mott 1964, Coles 1958).

1.3 The effect of non-magnetic impurities

Where two or more independent scattering mechanisms each contribute to a total resistivity one expects the resultant relaxation time and resistivity to be given by

$$1/\tau = 1/\tau_0 + 1/\tau_1 + \dots$$

$$\text{and } \rho = \rho_0 + \rho_1 + \dots \quad \dots (4)$$

Let ρ_1 be the ideal resistivity of a pure metal and ρ_0 the resistivity caused by the presence of a small proportion of impurities. The former is a function of temperature, but if the impurity atoms may be considered as obstacles of fixed scattering cross section, then ρ_0 is a constant. Under these circumstances $d\rho/dT$ at any temperature is independent of the impurity concentration. Such an effect was first observed by Matthiessen and Vogt (1864) and the fact that independent resistivities are additive has become known as Matthiessen's rule. It should be valid provided that there is no change in the effective number of free electrons and that the lattice constants of the host remains unaltered. Evidently there is always an upper limit of impurity concentration below which the rule may be applied, depending on the similarity of solvent and solute.

Considering an alloy system A B in which the A and B atoms have equal valency and atomic volume, Mott and Jones (1936) show that for small concentrations x , the resistivity increase ρ_0 is proportional to x , and that 1% of B dissolved in A produces the same extra resistivity as 1% of A in B. This is actually a special case of Nordheim's rule which states that over the complete range of compositions ρ_0 has the parabolic form $x(1-x)$, provided that the alloys are random and all of the same crystal structure. This is observed in silver-gold alloys.

If the solute atom has a different valency from the solvent, the impurity scattering is greater because of the charge difference Z between the host and impurity ions. Linde found empirically that ρ_0 is proportional to Z^2 for a given small impurity concentration, which may be understood by analogy with Rutherford scattering. A treatment by Mott using a screened coulomb potential at the impurity

$$V(r) = \frac{Z e^2}{r} e^{-q \cdot r}$$

leads to this dependence but gives too large a magnitude. A more accurate calculation has been made by de Faget et al. (1956) who considered the phase shift in the wavevector which an electron suffers on collision. If a central field potential V is substituted into the Schrodinger equation it may be shown (eg Mott and Sneddon 1948) that at large distances from the origin the phase shifted wave function of quantum number l has the form

$$\psi_{k,l} \propto \frac{1}{r} \sin(kr - l\pi/2 + \eta_l) P_l(\cos \theta)$$

where η_l is the l -th component of the phase shift. From this expression it is possible to derive an expression for the scattering cross section T

in terms of the phase shifts (Messiah 1961, Ziman 1960):-

$$T = \frac{4\pi}{k_F^2} \sum_l l \sin^2 (\eta_{l-1} - \eta_l)_{E_F} \quad \dots (5)$$

Thus the resistivity may be calculated if the phase shifts are known. To do this Friedel (1952) considered a large sphere of radius R and set $\Psi_{k,l} = 0$ at R thereby quantising the allowed states of the wave vector:

$$k_l = (\lambda + 1/2) \frac{\pi}{R} - \frac{\eta_l}{R} \quad \lambda = 0, 1, 2 \dots$$

There is thus one state every $\Delta k_l = \pi/R$ and since the change in k_l due to the central potential is η_l/R , the number of extra states introduced by the impurity is (allowing a $2(2l + 1)$ degeneracy) $2(2l + 1) \eta_l/\pi$. Summing this over l and equating it to the charge difference Z between the host and the impurity gives the Friedel Sum Rule

$$Z = \frac{2}{\pi} \sum_l (2l + 1) \eta_l$$

It is now necessary to choose a suitable form for the central potential so that the calculated phase shifts are consistent with this rule, and then to calculate the resistivity from equation 5. As Friedel shows (1956) the numerical agreement obtained for alloys of copper with Zn, Ga, Ge, and As is much better than in Mott's calculation.

A notable series of exceptions to Linde's rule is to be found in alloys of the noble metals with transition metal impurities in which the residual resistivities (the values as $T \rightarrow 0$) have a more

complicated behaviour due to the presence of d electrons. These and related effects form the subject matter of the rest of this chapter.

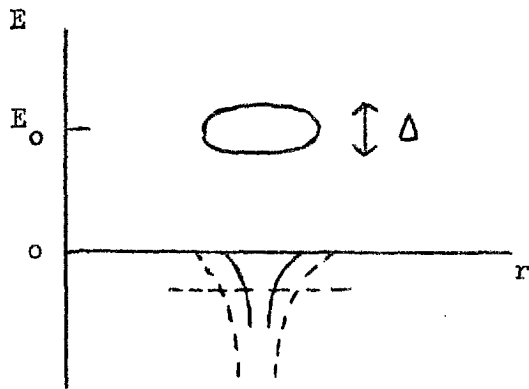
1.4 Resonant scattering: magnetic impurities

It was noted in section 1.2 that in transition metals the d electrons are neither wholly localised nor wholly itinerant. An analogous situation arises when a transition atom is dissolved in a 'simple' metal such as a noble metal. The potential at the impurity is not strong enough to bind the d state to the ion and the state therefore lies within the conduction band of the host at energy, say, E_0 . Here it resonates with the extended states of energy $\sim E_0$, giving rise to a new set of extended states which have a strong d component in the neighbourhood of the impurity. The sum of the amplitudes of all these components is equivalent to the charge excess introduced by the d state.

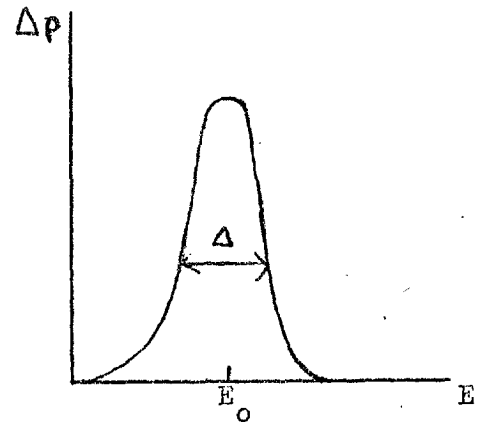
Alternatively the d state may be visualised as a 'virtual bound state' (vbs) within the conduction band, broadened by the resonance (fig 1.2 a). A conduction electron incident on the vbs spends a time $\sim \hbar/\Delta$ (where Δ is the vbs width) before re-emission as a scattered wave. The phase shift as a function of incident energy E is given by

$$\eta_1 = \tan^{-1} \left(\frac{\Delta}{2(E_0 - E)} \right)$$

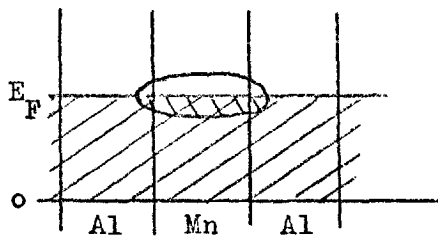
and reaches a maximum value of $\pi/2$ at resonance (when $E = E_0$) (Messiah 1961). Using equation 5 and neglecting the small phase shifts of components other than $l = 2$, the cross section for the resonant scattering may be calculated as a function of incident energy (fig 1.2 b). The only electrons able to contribute a resistivity, however, are those at the Fermi energy and resonant scattering will only be detected if



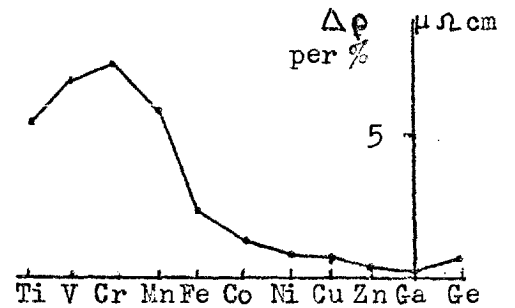
1.2a: Dashed curve: potential giving bound state
Full curve: potential giving vbs



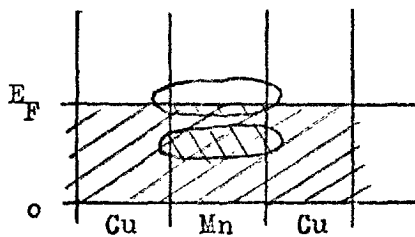
1.2b: Residual resistivity at Energy $E(=E_F)$ due to vbs



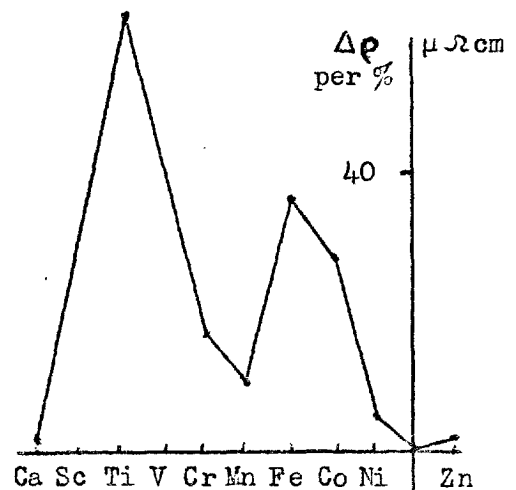
1.2c: vbs due to Mn in Al



1.2d: Residual resistivity due to 1% impurity in Al



1.2e: vbs due to Mn in Cu



1.2f: Residual resistivity due to 1% impurity in Cu

Fig 1.2. Nature of the vbs and its effect in residual resistivities (after Friedel 1958)

E_0 is sufficiently close to E_F . But the full complement of the vbs is 10 electrons and therefore for transition atoms the vbs must be only partially occupied and intersected by the Fermi level. A residual resistivity, whose magnitude reaches a maximum where the vbs is about half full (and $E_0 \sim E_F$), would be expected to result.

Of the 10 states in the vbs, five are of spin + and five are of spin -. In a half filled vbs it might be expected that exchange correlations between electrons would act, as in the free atom, to align the five spins parallel to one another. The vbs would in these circumstances be split into two halves, one half occupied while the other is empty and therefore located above E_F . However such a situation is only stable if the splitting is large compared with the vbs broadening. Friedel (eg 1958) estimated that the splitting condition would be fulfilled if

$$\Delta \leq p \, dE$$

where p is the number of d electrons in the vbs (up to 5) or holes (otherwise), and dE is the energy difference between the parallel and antiparallel alignment of two spins. Δ increases with the Fermi energy of the solvent, and the effect of the splitting may be seen by comparing the residual resistivities per percent of $3d$ solutes in copper ($E_F \sim 7$ eV) and aluminium ($E_F \sim 13$ eV). In the latter a single maximum in the residual resistivity is observed at Al Cr, indicating that here the vbs is unsplit and $E_0 \sim E_F$ (figs 1.2 c and d). In the former two peaks in the residual resistivity are observed corresponding to the maximum in the scattering due to each half of the split vbs (figs 1.2 e and f).

If the vbs is split, the numbers of occupied states of each spin are not equal and therefore the impurity possesses a localised moment. Confirmation of the results for the resistivities may

therefore be sought from magnetic susceptibility data. It is found that Cu Cr, Cu Mn and Cu Fe all show a Curie-Weiss susceptibility indicating the presence of magnetic moments, while Al Mn, Al Cr, Cu Ni do not. These results show that the vbs concept is able to provide at least a semi-quantitative model of the magnetic impurity. A more rigorous treatment follows.

1.5 The formation of the local moment.

In the last section the virtual bound state splitting in copper was examined as the number of d electrons on the impurity was increased. Matthias et al. (1960) and Clogston et al. (1962) investigated the formation of moments by measuring the susceptibility of alloys in which the impurity was always 1% Fe but the hosts were metals and binary alloys of the 4 d transition series. They observed that iron is non-magnetic in Nb but magnetic in Mo with an effective moment $p \sim 2 \mu_B$ (μ_B is the Bohr magneton) obtained from the Curie-Weiss law (at $T > \theta$)

$$\chi = n p^2 / 3k_B (T - \theta) \quad \dots (6)$$

where n is the number of impurities and θ is the Curie temperature. The moment is again zero in 5 d rhenium (substituted for 4 d technetium) but reappears between ruthenium and rhodium, and becomes very large in rhodium-palladium alloys. The appearance of the moment in both Nb Mo and Ru Rh was shown to be remarkably rapid; in the former it was not observed until the alloy contained 60% Mo but was fully established in pure Mo. While the relatively low density of states at this point in the d band is probably the major factor in reducing the vbs width and causing it to magnetise, the Friedel theory does not account for the sharpness of the effect.

A similarly sudden appearance of a moment on iron impurities was later observed in the simpler host Cu Zn as the copper content was

increased from 14 to 21%. The effective moment observed from susceptibility measurements (Caplin et al. 1968) increased from below $0.3 \mu_B$ to $\sim 1.4 \mu_B$, and in this system there can be no uncertainty arising from the presence of a d band.

To account for this behaviour, Anderson (1961) proposed the following model. A d state at an impurity, containing for simplicity one electron is initially magnetised; ie the state of spin +, say, is occupied ($n_{d+} = 1$) at energy E which the corresponding state of spin - is empty ($n_{d-} = 0$) and therefore above E_F . The separation between the two is U , the Coulomb repulsion between the two states. The d levels resonate with the extended states, as expressed by a mixing interaction V_{kd} , and are broadened. If the broadening Δ is sufficient and U is not too large, the spin + and spin - states overlap and the spin - state becomes partially occupied. If δn is the change in occupation the effective Coulomb repulsion is reduced to $U(1-2\delta n)$. The splitting of the levels is therefore reduced and the overlap further increased. The process may snowball until the impurity is completely demagnetised ($\delta n = 0.5$), or if U is sufficiently large compared with Δ , the state may remain magnetic but with a reduced moment, as shown in fig 1.3.

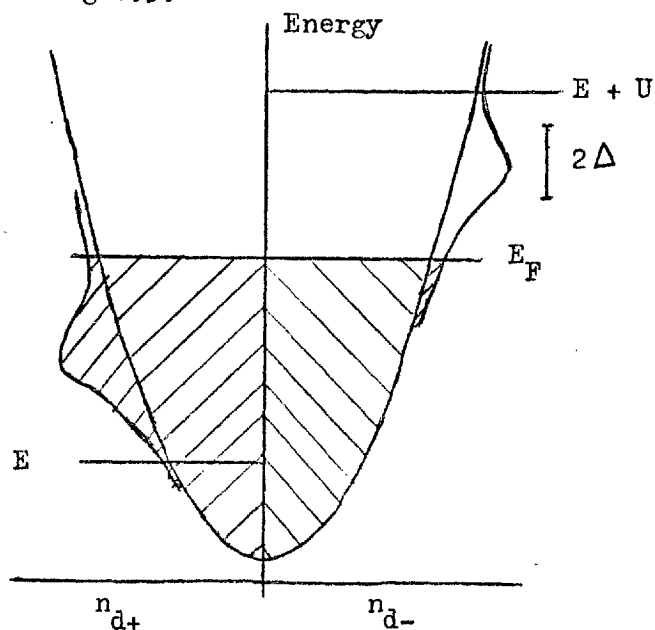


Fig 1.3. Density of states, showing a magnetised vbs (Anderson 1961)

Anderson calculated the occupation indices $\langle n_{d+} \rangle$ and $\langle n_{d-} \rangle$ in terms of E , E_F , U and $\Delta \left[= \pi \langle V_{kd}^2 \rangle N(E) \right]$ in a Hartree-Fock approximation using a Hamiltonian which included U and V_{kd} . He obtained

$$\langle n_{d+} \rangle = \frac{1}{\pi} \cot^{-1} \left[\frac{E - E_F + U \langle n_{d-} \rangle}{\Delta} \right]$$

and an identical expression for $\langle n_{d-} \rangle$ in terms of $\langle n_{d+} \rangle$. These must be solved simultaneously, given relative values for the energies involved. If for simplicity it is assumed that the state is split symmetrically about the Fermi level, ie $E_F - E = U/2$, then the solutions are completely determined by U/Δ . For a ratio ~ 1 the only solution occurs at $\langle n_{d+} \rangle = \langle n_{d-} \rangle = 0.5$ and the state is non-magnetic, but if it is increased above a critical value $U/\Delta = \pi$, two further solutions (identical but with interchange of spin directions) appear in which the occupations are not equal and a magnetic moment is supported.

Generalisation to states with more than one d electron does not alter the essential result, and Anderson was able to show that in alloys of 3 d solutes in copper where $U \sim 10$ eV and $\Delta \sim 2$ to 5 eV, transitions from non-magnetic to magnetic states could occur as the solute is varied. It is also plausible that the reduction in the density of states between niobium and molybdenum by a factor ~ 2 could precipitate a magnetisation of the vbs at an iron impurity. However, the d state is assumed to be a localised extra orbital, orthogonal to the conduction electron states with which it resonates via V_{kd} . It is not obvious that this 'dissolved ion' picture is realistic in cases where both host and impurity are transition elements. In a collective band treatment due to Wolff (1961), the vbs appears as a maximum in the scattering cross section for Bloch waves incident on the impurity, and may be split by

an exchange interaction if it is narrow enough and near enough to E_F . This is a more logical development of Friedel's work and though the conclusions are similar to Anderson's, the two models are based on different premisses. The relationship between them has been discussed by Rivier and Zitkova (1971) who were able to obtain the Anderson extra orbital from the scattering of Bloch electrons by the impurity. They developed a non-orthogonal Anderson model and found that as the orthogonality was reduced (ie the overlap between the extra orbital and the extended states was increased) the scattering became weaker and the system proceeded towards the 'Wolff limit' representing complete overlap and non-resonant scattering only. Evidence of this transition may be seen in resistivity-temperature data for alloys of rhodium with 0.5% Cr, Mn, Fe and Co, which are presented in Chapter 3. Rh Cr shows a resistance minimum characteristic of resonant scattering, while in the other three alloys the magnitude of the impurity resistivity falls both with temperature and as the solute progresses through Mn and Fe to Co, at which point the solute is isoelectronic with the solvent and the Wolff limit is reached.

1.6 The resistance minimum phenomenon

The first observation of a negative temperature coefficient of resistance at low temperatures in some nominally pure metals - Mg, Mo, Pd - was made by Meissner and Voigt (1930) and shortly afterwards it was found (de Haas et al. 1933) that the resistances of various 'pure' gold wires exhibited minima at temperatures ($\sim 4-10$ K) which seemed to be correlated with the resistance ratio $R_{\min}/R_{293}$. They concluded that the effect was due to an impurity, probably iron. However, it was not until the 1950s that systematic investigations were made from which a pattern of the nature and occurrence of the anomalies could be built up. A typical example of how a small quantity of impurity

can affect the resistivity of metals at low temperatures is given by the measurements of Gerritsen and Linde (1951 a) on dilute Ag Mn (fig 1.4). At very low concentrations where each Mn atom may be considered as an independent scattering centre, the impurity resistivity was found to have a negative temperature coefficient and was roughly proportional to the concentration. Added to the resistivity of pure silver, ρ_{Ag} , this produced the minimum at the point T_{min} where the temperature coefficients of each contribution were equal and opposite. T_{min} therefore rose as the Mn content was increased, though only slowly since ρ_{Ag} is approximately proportional to T^5 . At still quite a low concentration ($\sim 0.05\%$) Gerritsen and Linde found a resistance maximum at $\sim 1K$, but T_{max} rose rapidly with increasing concentration. At 0.4% Mn, T_{max} and T_{min} were both at $10-12 K$ and at higher concentrations still the temperature coefficient remained positive over the whole range.

A comprehensive review of resistive and other properties of dilute alloys with full references to the data available in 1963 was published by van den Berg (1964) and only the more important and recent results will be mentioned here. Particularly striking is the table adapted from Blandin and Friedel (1959) showing which of the alloys of Cu, Ag, Au, Zn, Mg and Al with small quantities of iron group transition metals give resistance minima at low temperatures (table 1.1). The most favourable combination is a host with a low Fermi energy E_F , and a solute in the middle of the transition series. Thus Cr, Mn or Fe in Au, Ag or Cu all give anomalies while Ti and Ni do not. In Au V and Au Co the effects are much smaller, and in Al Mn and Al Cr no effects were observed until the precise measurements of Caplin and Rizzuto (1968) were made. In this table the correlation between the appearance of the resistance minimum and the splitting of the vbs is noteworthy.

Rather less information is available on the effects of impurities of the second and third series transition elements although Au Mo and

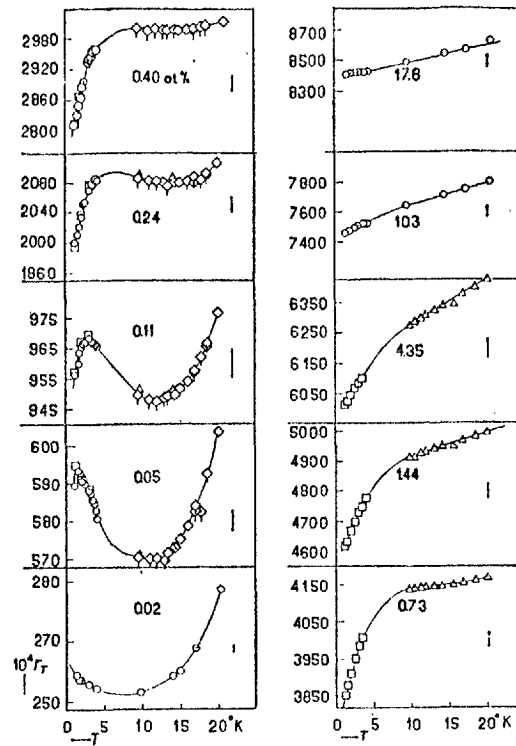


Fig 1.4 Resistance ratio $r_T = R_T/R_{293}$ in alloys of Ag-Mn of concentrations as indicated
(after Gerritsen and Linde 1951 a)

Solvent Solute	E_F eV	Au	Ag	Cu	Mg	Zn	Al
		5.5	5.5	7	7.5	9.5	13
V		*					
Cr		+		+			*
Mn		+	+	+	+	+	*
Fe		+	+	+	+	*	-
Co		*		*			-
Ni		-		-		-	-

Table 1.1: Occurrence of resistivity minima in alloys
(after Blandin and Friedel 1959)

- + deep resistivity minimum
- * shallow resistivity minimum
- normal residual resistivity

Au Os have been found to show resistance minima which were apparently not due to residual 3 d impurities (Knook and van den Berg 1963).

Alloys in which transition metals are both solute and solvent are particularly relevant to this thesis. In the 3 d series Cr, Mn and Fe in titanium give resistance minima (Hake et al. 1962) and the present work has revealed minima and maxima in some binary V-Cr hosts with up to 8% Fe (chapter 5). The 4 d series as hosts give more variety: normal behaviour in Nb Fe and Ru Fe, a minimum and a maximum in Mo Fe, an anomalous resistivity with positive temperature coefficient in Rh Fe and ferromagnetism even at low concentrations in Pd Fe (Coles 1963 and 1964). The remaining sections of this chapter review the theories and experiments which led to the reconciliation of such apparently disparate effects.

1.7 Allied phenomena

Anomalous effects in dilute alloys are not confined to the electrical resistivity. It would be surprising if other transport properties were immune, and indeed giant thermopowers, negative magnetoresistances and anomalous increases in thermal resistivity have all been observed in various alloys (see van den Berg 1964). Specific heats also show anomalies: a large linear term due to an extra density of states at E_F , and in some cases a peak at low temperatures. The link between these effects is that they are all associated with the presence of transition element impurities, and therefore magnetic properties are of particular interest.

Owen et al. (1956, 1957) measured the susceptibilities of Cu Mn, Ag Mn and Mg Mn and found that the impurity contribution approximately followed a Curie-Weiss law (eq 6) from which an effective moment of $\sim 5-6 \mu_B$ could be deduced, in good agreement with their electron spin resonance values. The results of Vogt and Gerstenberg (1959) for

Au Ti, however, showed that the susceptibility was practically temperature independent. Evidence gradually accumulated that the resistance minimum is only observed in alloys in which the impurity atoms carry a localised magnetic moment. The correlation was clearly demonstrated by Sarachik (1964) who measured the resistivities of a series of (Nb-Mo) Fe alloys in which the host composition was varied, and found that the minimum appeared at about 60% Mo just where Clogston et al. (1962) had first encountered a Curie-Weiss susceptibility. A closer correlation was observed by Caplin et al. (1968) in the (Cu-Zn) Fe system in which the magnitude of the effective moment on the iron atoms increased in the range 14-21% copper in a manner paralleled by a marked deepening of the resistance minimum.

The presence of localised moments allows an explanation of the negative magnetoresistance if the scattering of conduction electrons is spin-dependent. Ziman (1960) shows that the magnetoresistance contains a term

$$- A (n_+ - n_-)^2 / (n_+ + n_-)$$

which is always negative and proportional to the square of the magnetisation. The observed effect can be large (Gerritsen and Linde (1951 b) found a -26% change in resistance in Ag 0.05% Mn at a field of ~22 K Gauss and at ~4 K) and is in good accord with this law (Schmitt and Jacobs 1957).

The thermopower of a metal or alloy is given by

$$Q = - \frac{\pi^2 k_B^2 T}{3 e} \left[\frac{\partial \ln \rho(E)}{\partial E} \right]_{E_F}$$

(Ziman 1960) and is therefore very sensitive to changes in the surfaces of constant energy near E_F and to changes in the density of states in

this region. Thus the positioning of a vbs near E_F whether magnetised or not may have a large effect on Q . MacDonald et al. (1962) measured the thermopowers of alloys of gold with 0.2% Cr, Mn, Fe, Co and Ni impurities and found 'giant' thermopowers of $\sim 12 \mu\text{V/K}$ at 16 K in Au Fe and Au Co, while Cr, Mn and Ni produced effects $\sim 2 \mu\text{V/K}$ which may still be classified as 'large'. This is consistent with the view that the vbs for both Fe and Co presents a large scattering across section at E_F and so probably a large $(\partial \ln \rho / \partial E)$, larger than Mn or Cr where the vbs is well split, or Ni where it is nearly full.

Even before the connection between localised moments and the resistance minimum had been established, the observation of the resistance maximum had been associated with the onset of magnetic order, for a number of reasons. Firstly T_{max} rises as the concentration increases, ie as the average distance between solute atoms decreases and the magnetic interactions increase. Secondly Owen et al. (1956) found that the susceptibility of Cu Mn passed through a broad maximum at $T \sim \theta$, and θ , like T_{max} , increased with concentration. However the positive value of θ , the hysteresis in the magnetisation versus field curves and remanence effects suggested that the ordered state was not a simple antiferromagnet. Thirdly the specific heat anomaly is indicative of an ordering process. Martin (1963) drew a distinction between alloys in which only a resistance minimum is observed and those in which a maximum is also found. In the former, eg Cu Fe, the temperature of the maximum in the excess specific heat is roughly independent of temperature (Frank et al. 1961), while in the latter, eg Ag Mn (de Nobel and du Chatenier 1959), it occurs at approximately the temperature of the resistance maximum and rises with increasing concentration. Although both cases give an anomaly there seems no doubt that where a resistance maximum is found, it is associated with ordering.

The nature of the ordering, however, is complicated. If the magnetisation of Cu Mn is measured with increasing temperature after cooling in zero field, a maximum is found at $\sim \theta$ K. If, however, it is measured as the sample is cooled in a constant magnetic field, the magnetisation rises to its maximum value at $\sim \theta$ but remains roughly constant as the temperature is lowered further (Beck 1971). Remanence is also observed in zero-field cooled samples below θ (Schmitt and Jacobs 1957); if a field is applied and then removed a small magnetisation persists which, however, decays with time under thermal activation. Thus although the transition resembles an antiferromagnetic one, the positive θ determined from the high temperature susceptibility, and the remanence suggest ferromagnetic interactions between manganese ions. The phenomenon has found an explanation in terms of short range order in which the interaction is of the Rudermann-Kittel-Kasuya-Yosida (RKKY) type first applied to Cu Mn by Yosida (1957). The conduction electrons near the impurity are polarised by the s-d exchange correlation and the magnitude of the polarisation dies away in an oscillatory manner with increasing distance from the impurity. A second impurity a distance r from the first feels the polarisation and there is an effective interaction via the conduction electrons given by

$$F(x) \propto \frac{x \cos x - \sin x}{x^4}$$

where $x = 2 k_F r$. This can extend over a relatively long range and even in dilute Cu Mn (0.05% Mn) can produce a coupling which is either ferromagnetic or antiferromagnetic depending on the sign of $F(x)$. Thus in a random alloy no consistent pattern of order is observed over large distances and at lower temperatures the spins are apparently 'frozen in' at random. In a field-cooled sample the magnetisation may be expected to be frozen in also and to decay only gradually. A

system which exhibits this short range order is said to be a 'spin glass' (also micromagnetic), the randomness of the spin orientations being analogous to the amorphous structure of glass.

1.8 The Kondo theory of the resistance minimum

In the last section experimental evidence was described, showing that the resistance minimum is observed only in alloys in which local moments are established, and it is now necessary to investigate the connection theoretically. The treatment is due to Kondo (1964), and the term 'Kondo Effect' is now applied to the resistance minimum and other manifestations of isolated local moments in metals.

Kondo calculated the probability of a conduction electron being scattered by a magnetic impurity using a Hamiltonian for the direct s-d exchange interaction which was later shown to be equivalent to Anderson's Hamiltonian for the mixing term V_{kd} (Schrieffer and Wolff 1966). Considering only the direct transition $k_+ \rightarrow k'_+$ leads to a temperature independent resistivity, but Kondo took the calculation to second order by including scattering routes via an intermediary state q_+ . There are four possibilities for $k_+ \rightarrow k'_+$:-

- (i) $k_+ \rightarrow q_+ ; q_+ \rightarrow k'_+$
- (ii) $q_+ \rightarrow k'_+ ; k_+ \rightarrow q_+$
- (iii) $k_+ \rightarrow q_- ; q_- \rightarrow k'_+$
- (iv) $q_- \rightarrow k'_+ ; k_+ \rightarrow q_-$

where the two steps are written in order of occurrence. There are also four similar scattering possibilities in which the final state is k'_- . The scattering amplitude for route (i) contains a Fermi factor $(1 - f_q)$ expressing the requirement that state q_+ should initially be empty ($0 \leq f_q \leq 1$ gives the occupation probability).

The amplitude for route (ii) is the same as for (i) except that the Fermi factor is just f_q since q_+ must initially be occupied. When these two amplitudes are added f_q drops out and the remainder is small and temperature independent. The amplitudes for routes (iii) and (iv) contain the Fermi factors in the same way but for each transition the spin operator S_+ or S_- must be included, depending on the change of spin accomplished. The order in which these operators appears is different in (iii) and (iv) and when these amplitudes are added the Fermi factor remains, multiplied by the spin commutator:-

$$(S_+ S_- - S_- S_+) f_q .$$

This is not zero and the total scattering amplitude involves f_q which approximates to a step function at $q = k_F$ at low temperatures. Kondo showed that this leads to a divergence in the scattering amplitude and a resistivity of the form

$$\rho_{\text{spin}} = \text{const} \left[1 + (3Z J/E_F) \log T \right]$$

where J is the exchange coupling constant and Z the valence difference. If J is negative ρ_{spin} rises as T falls and therefore at low temperatures where the impurity resistivity dominates, a resistance minimum is produced. This logarithmic law was found to fit the experimental data for Cr, Mn, and Fe in Au and Cu over a wide temperature range (Heeger 1969 p 347), but Kondo's suggestion that the decreasing resistivity of Rh Fe might be due to a positive exchange coupling, while in considerable agreement with the results, is difficult to reconcile with the negative θ deduced from susceptibility measurements.

The more important difficulty with the theory is that the logarithmic divergence to ∞ at $T = 0$ is not physically allowable. A more complete calculation by Abrikosov (1965) including transitions from

k_+ to $k'_\pm$ by any indirect scattering route led to a resistivity

$$\rho_{\text{spin}} = c \rho_0 \left[1 - 2J N(E_F) \ln(k_B T/D) \right]^{-2}$$

For $J < 0$ the divergence is still present but has been shifted to a temperature given by

$$k_B T_K = D \exp \left[-1/2 |J| N(E_F) \right]$$

This expression is reminiscent of that for the superconducting critical temperature and suggests that below T_K there is a condensation into a ground state which is inaccessible to perturbation theory. Such a state was postulated by Nagaoka (1965) to consist of the impurity spin surrounded by a cloud of polarised conduction electrons whose net spin just compensates that of the impurity. The state is then a non-magnetic singlet and the resistivity according to Nagaoka should fall away from the Kondo $\log T$ with the form $(1 - AT^2)$. As Schrieffer (1967) pointed out, there is no sharp phase transition as the effect is a localised non-cooperative one. Furthermore it is broadened by thermal fluctuations and the change in regime may occupy a wide temperature range. Schrieffer also suggested that due to the exponential dependence of T_K on J , small changes in the coupling may shift T_K by many orders of magnitude. Thus alloys which on the Anderson model are magnetic (low V_{kd} , narrow vbs compared with U) are characterised by a low T_K , while in non-magnetic alloys (large V_{kd}) T_K is high. In the latter case the spin compensated state is encountered at 'normal' temperatures, but a transition to a magnetic state might be expected if the temperature is raised sufficiently (provided that the melting point is not reached).

Experimentally it is not easy to obtain data for a given alloy extending from $T \ll T_K$ to $T \gg T_K$ because of the broad transition

region. In Au Fe and Cu Mn where $T_K \ll 1$ K, it is difficult to separate a real effect of spin compensation from the effect of interactions between impurities which may be significant at very low temperatures even for small concentrations. Evidence for the formation of the Nagaoka state in Cu Mn has been obtained, however, using the specialised technique of nuclear orientation (Campbell et al. 1967) from which a Kondo temperature of ~ 0.06 K was deduced. In Cu Fe $T_K \sim 20$ K and the range below T_K is convenient for resistivity measurements as the ideal resistivity of pure copper and deviations from Matthiessen's rule are small. Star et al. (1972 a) obtained a good fit to the $(1 - AT^2)$ law at $T \ll T_K$ although even at 30 ppm Fe interaction effects were observable below 0.3 K. Al Mn, non-magnetic according to Friedel and Anderson, now appears as a high T_K system ($T_K \sim 530$ K), and the $(1 - AT^2)$ resistivity has been observed in the helium range (Caplin and Rizzuto 1968). Similar results were obtained for Au V ($T_K \sim 300$ K, Kume 1967) though Star et al. (1972 b) found deviations from the law, ascribed to iron impurity.

There have been many treatments of the Kondo effect for $T \ll T_K$ apart from Nagaoka's and these are reviewed by Kondo (1969), Heeger (1969) and Star (1971). Only the localised spin fluctuation theory will be discussed here as it is applicable both to 'Kondo alloys' and the Rh Fe anomaly, and is therefore conveniently used in discussing the experimental results of this work.

1.9 Localised spin fluctuations

The Friedel-Anderson virtual bound state was found to be magnetic or non-magnetic depending on whether $U/\pi\Delta$ is greater or less than unity. Time played no part in the model, except that the vbs width implicitly limits to $\hbar \Delta^{-1}$ the time for which an electron is localised at the impurity. Rivier and Zuckermann (1968 and 1969) proposed that

the dynamical nature of the vbs should be recognised and invoked the concept of localised spin fluctuations (lsf) which had been introduced into the theory of nearly ferromagnetic metals and alloys (see next section). Suppose at a given time a d electron, d_+ , of spin + occupies a localised state of energy E at an impurity and that the corresponding state of opposite spin, d_- , is unoccupied (at energy $E + U > E_F$). There is a repeated scattering between these states and the occupied state is alternately d_+ and d_- . The impurity appears in an experiment to be magnetic only if the lifetime of this spin fluctuation τ_{sf} is long compared with thermal fluctuation times, ie if

$$\tau_{sf} \gg (k_B T)^{-1} \quad (\text{with } \hbar = 1).$$

Thus at high temperatures the spin appears to be long lived and the moment well established, while at low temperatures where this condition is not fulfilled, the spin fluctuations are relatively rapid (though τ_{sf} is unchanged) and the impurity is apparently non-magnetic. Rivier and Zuckermann argue that this is a simpler and more acceptable postulate than Nagaoka's spin compensated state, though the consequences are the same. They propose that the essential difference between Mn in Al and Mn in Cu is that in the former the spin fluctuations are faster than in the latter, and that the Kondo temperature for a given alloy is conveniently defined by

$$k_B T_K = \tau_{sf}^{-1}.$$

In terms of the parameters of the Anderson model, they deduce that

$$\tau_{sf} = \pi N_d(E_F) \left[1 - U N_d(E_F) \right]^{-1}$$

where $N_d(E_F) = \Delta \left[\pi (E_d^2 + \Delta^2) \right]^{-1}$ is the d electron density of states at E_F and E_d is the energy of the d state relative to E_F . Caplin and Rizzuto (1968) show the significance of this expression in their discussion of lsf in Al Mn. In the case where U/Δ and E_d are small and there is a non-magnetic vbs, then τ_{sf} is small and $\sim \Delta^{-1}$. At a finite temperature, fluctuations $\sim k_B T$ occur in the relative positions of the d + and d - states. The effect of a Coulomb repulsion is to increase the amplitude and duration of these fluctuations by an amount

$$\eta = \left[1 - U N_d(E_F) \right]^{-1}.$$

Thus as U/Δ increases, the spin fluctuation lifetime becomes longer. the singularity in the expression arises from the use of the Hartree-Fock approximation which is strictly only valid in the absence of electron-electron correlations (non-magnetic limit). A more reasonable expectation is that $\tau_{sf} \rightarrow \infty$ as $U \rightarrow \infty$, and this emerges from rigorous treatments (see Heeger 1969 p 301).

Experimentally the lsf model has been most thoroughly tested in Al Mn and Al Cr. Caplin and Rizzuto found that the low temperature resistivity could be described by a $\left[1 - (T/T_K)^2 \right]$ law as predicted by Rivier and Zuckermann and deduced $T_K \sim 530$ K and 1200 K for the two systems. These values are in reasonable agreement with measurements of the susceptibilities which are Pauli paramagnetic, enhanced by the factor η . In a more recent development of the theory Rivier and Zlatić (1972 a) derive a universal curve in which the quadratic resistivity region and the Kondo log T region are bridged by a $(1 - BT)$ dependence. This linear region has been observed in Al Mn by Babic et al. (1972) and Kovacs-Csetenyi et al. (1972) between 150 K and 300 K, but no log T region has yet been seen.

1.10 Exchange enhanced hosts

The theories described in the last few sections have been found to give a reasonable account of the experimental observations of alloys in which a transition element is dissolved in a simple host. In addition it was possible to interpret the results of Matthias et al. for (Nb-Mo) Fe in terms of the Anderson model in spite of the presence of an approximately half-filled d band, and the resistivity measurements of Sarachik et al. on that system showed that where iron is magnetic, a Kondo minimum is observed. Iron dissolved in rhodium or palladium, however, does not conform to this picture, and these and similar alloys are now discussed.

Although pure palladium is Pauli paramagnetic, its susceptibility is about ten times greater than χ_0 , the value calculated using the density of states $N(E_F)$ obtained from a measurement of the electronic specific heat. This discrepancy is due to the Coulomb correlation U which acts within an atomic cell to separate d electrons of opposite spins. A thermally excited fluctuation in the local spin density is enhanced as a result of this interaction by a factor $[1 - U N(E_F)]^{-1}$. It is therefore deduced (see Lederer and Mills 1968) that in palladium $U N(E_F) \sim 0.9$ so that $\chi \sim 10 \chi_0$ and the pure metal is close to the Stoner criterion $U N(E_F) = 1$ for the onset of itinerant ferromagnetism. Similar considerations lead to an enhancement factor $\sim 5/3$ in Pt and between 1 and $5/3$ in Rh, while in nickel the correlation is so strong that ferromagnetism results.

When nickel is dissolved in small quantities in palladium, with which it is isoelectronic, it does not give rise to a local moment. However the exchange enhancement factor is increased and at a low concentration ($\sim 2-3\%$) long range ferromagnetism sets in. Resistivity measurements give a good indication of this. Lederer and Mills (1968) show that the scattering of s electrons from localised spin

fluctuations in the d band is proportional to T^2 and that the effect is larger than Baber scattering which is spin independent. Schindler and Rice (1967) found that the resistivity of pure palladium is indeed proportional to T^2 below 10 K, and that the addition of 1% Ni increases the coefficient of the T^2 term by a factor of 10. Later detailed results of Tari and Coles (1971) showed that as the critical composition is approached the exponent falls from 2 to ~ 1.5 but the coefficient continues to rise and exhibits a sharp peak which enabled them to determine the critical composition as $2.32 \pm 0.03\%$ Ni.

By contrast Pd Fe and Pd Co exhibit local moments whose effective moments obtained from susceptibility measurements are large - $12 \mu_B$ and $10 \mu_B$ respectively. These 'giant' moments can be understood by assuming that a polarisation is induced on near neighbour palladium atoms, and this is consistent with the observation of transitions to ferromagnetism at low concentrations; eg Pd with 0.1% Fe is ferromagnetic at 1 K (Coles et al. 1965). In Pd Mn the moment, $5.6 \mu_B$, is more nearly that which would be predicted for a bare Mn ion though some polarisation is evidently present as ferromagnetism sets in at about 4 K in a 1% alloy (Sarachik and Shaltiel 1967, Williams and Loram 1969). However these systems are not describable as Kondo alloys. The local moments arise from the exchange enhancement in the palladium d band and the resistivity above the ordering temperature is more appropriately described by the Lederer and Mills theory of scattering from spin fluctuations in the d band rather than in an impurity vbs. As the impurity moves further to the left in the periodic table, to Cr, this collective band approach becomes untenable. In Pd Cr the resistivity exhibits a minimum which at low temperatures has the form $(1 - A T^2)$ giving a Kondo temperature $T_K \sim 280$ K (Star et al. 1972 c). Thus the Cr impurity would appear to form a virtual bound state of the Friedel-Anderson type.

Broadly similar results are obtained for 3 d solutes in platinum though the exchange enhancement of the host is smaller and the effects are less dramatic - Pt Ni is ferromagnetic only for more than 40% Ni (Schindler 1970), while a Pt Fe alloy with 1% Fe orders at ~ 4 K (Loram et al. 1972). A resistance minimum is observed in Pt Cr and a Kondo temperature of 460 K was deduced by Star. In rhodium the transition from the collective band system (Rh Co) to the Friedel-Anderson vbs and resistance minimum of Rh Cr has already been noted (section 1.5), but the resistance anomaly most evident in Rh Fe does not conform to the Lederer-Mills theory. A similar effect was observed in Ir Fe (Sarachik 1968), and later in paramagnetic Pd Co, Pt Co and Pt Fe (Loram et al. 1971 and 1972). At low temperatures, however, the resistivity of Ir Fe is proportional to T^2 , and by extending the Lederer and Mills model to higher temperatures Kaiser and Doniach (1971) were able to account for many anomalous features in this class of alloys. In view of the importance of Rh Fe in the present work, this system will be discussed in detail in the next section.

1.11 The resistivity of rhodium-iron

The impurity resistivity in Rh Fe was found (Coles 1964) to have a very large temperature dependence of a character that had not previously been observed in any other system. From 1 K to 50 K its magnitude increased by a factor of about 3 and the curvature was such that the slope was largest at low temperatures, gradually diminishing as if to become zero at high temperatures (fig 3.1). Since the impurity resistivity was found to scale well with concentration up to 0.85% Fe, the effect is clearly not associated with the effects of interactions between iron atoms, but is the result of conduction electron scattering from isolated impurities. In the original experiments the magnetoresistance below 4.2 K was found to

be normal and in accordance with Kohler's rule, while the thermopower was large ($-4 \mu\text{V/K}$ in the helium range) though not 'giant' as in Au Fe. Clogston et al. (1962) deduced from susceptibility measurements that the iron atoms carry a magnetic moment of $2 \mu_B$. Closer investigations however showed (Coles et al. 1965, Knapp 1967a) that in fact the Curie-Weiss law does not give a good fit to the data over a wide range of temperature: the values of the effective moment and Θ depend on the range in which the fit is attempted, and both apparently decrease as the temperature falls. From Knapp's results the values of Θ obtained below 40 K are independent of concentration, which again suggests the absence of interaction effects.

An early attempt to describe the resistivity theoretically was made by Kondo (1964) in his paper on the resistance minimum (1.6). He suggested that in his theory a system in which the s-d exchange coupling is positive would exhibit a resistivity proportional to $+\log T$ and found that such an expression fitted the Rh Fe data quite well except at low temperatures. However the susceptibility measurements show that Θ is negative and therefore that J is negative in Rh Fe. To circumvent this difficulty Kondo (1968) developed a calculation in which the normal potential scattering was found to modify the 'spin flip' resistivity to $(\text{Const. } J \cos 2\eta \log T)$ where η is the potential scattering phase shift. Thus a positive $\log T$ resistivity may be consistent with a negative J provided that η lies between $\pi/4$ and $3\pi/4$. The difficulty now, as Star (1971) and Loram et al. (1972) point out, is that the Rh Fe effect is observed in just those systems where the valence difference is small and therefore η is expected to be small.

Another phenomenological explanation for the effect was based by Knapp (1967 b) on an analysis of his susceptibility data for Rh Fe

and also for Ir Fe. These may be fitted to a Curie law by allowing the effective moment to decrease with temperature to 0 at $T = 0$. Knapp suggested that the host d band is responsible for a Nagaoka condensation so that the current-carrying s electrons are less and less scattered by the impurity as the moment is compensated, and the resistivity falls with temperature. Unfortunately such a model does not allow a mechanism for the anomalous thermopower and therefore cannot be substantiated.

The resistivity of Ir Fe (Sarachik 1968) shows a similarity with both Pd Ni and Rh Fe. The impurity resistivity $\Delta\rho$ decreases with decreasing temperature as in Rh Fe down to 50 K, below which an extended region is encountered in which $\Delta\rho \propto T$. Below 10 K $\Delta\rho$ flattens out to resemble the T^2 dependence found in Pd Ni. These results suggest that the same scattering mechanism may be responsible for the anomalies in all three systems, but that as in Kondo alloys there is a different characteristic temperature in each case. Thus in Pd Ni the T^2 dependence dominates the results up to 20 K while in Rh Fe no T^2 term is observed down to 1 K. The scattering of conduction electrons from localised spin fluctuations in the d band was found by Lederer and Mills (1968, see section 1.10) to give a T^2 resistivity at low temperatures, and Kaiser and Doniach (1971) extended this calculation to cover all temperatures. The resistivity is a function of the coupling constant between the conduction electrons and the lsf, the Bose factor giving the number of lsf excitations at a given temperature, and the lsf spectral density $A(q, \omega)$ in which q and ω are the lsf wavenumber and frequency. The evaluation of $A(q, \omega)$ in turn requires a knowledge of the generalised host susceptibility $\chi(q, \omega)$. Using averages over q ,

$$A(q, \omega) \rightarrow \bar{A}(\omega)$$

$$\text{and } \chi(q, \omega) \rightarrow \bar{\chi}_R + i \bar{\chi}_I,$$

Kaiser and Doniach were able to define an enhancement factor for the 1sf, $\alpha = (1 - \delta U \bar{\chi}_R)^{-1}$ where δU is the increase in the coulomb repulsion at the impurity above that in the host, and a spin fluctuation temperature given by $k_B T_s = (\alpha \delta U \bar{\chi}_T / \omega)^{-1}$. $\bar{A}(\omega)$ is then found initially to increase linearly with ω up to a peak at energy $k_B T_s$ and at high energy to decrease as $1/\omega$. The curve is a universal one, whose scale is determined by α . It allows an equation to be derived for a scaled resistivity as a function of reduced temperature T/T_s which Kaiser and Doniach show is proportional to $(T/T_s)^2$ in the limit of low temperatures (as found by Lederer and Mills) and linear with T above $T_s/4$ (as expected for scattering by bosons - eg phonons). The expression for the resistivity is, however, universal only if the scaling factors are independent of temperature. But if α is large it is very sensitive to a small temperature dependence in $\bar{\chi}_R$. Kaiser and Doniach found that $\bar{\chi}_R$ tends to decrease as the temperature increases. Thus $\alpha(T)$ decreases and T_s increases with temperature, and the resistivity is expected to fall below the universal curve at high temperatures.

As expected the model may be applied to dilute Pd Ni alloys and Kaiser and Doniach deduce $T_s \sim 76$ K in this system. The T^2 region extends to ~ 20 K but at 30 K, the high temperature limit of the Schindler and Rice (1967) data, the resistivity has already fallen below the linear law.

The most detailed comparison of the model with experiment is for Ir Fe, where the data give a good fit with $T_s \sim 28$ K. The temperature dependence of T_s and so of $\alpha(T)$ may be calculated from the depression of the resistivity below the linear law which occurs at temperatures above 30 K. Kaiser and Doniach compare $\alpha(T)$ obtained in this way with Knapp's results for the static susceptibility and show that there is a good correlation between the two.

Rh Fe presents greater problems. In agreement with the predictions of the theory, the T^2 dependence of the resistivity has been observed below 1 K, though T_s is apparently concentration dependent (see chapter 3). The linear region, however, is not clearly established and it is necessary to assume that the temperature dependence of the enhancement factor modifies the Kaiser-Doniach curve at all temperatures above 2 K. Since the functional form of this modification is not predicted, the theory can only give a qualitative description of the Rh Fe resistivity for most of the range.

It was noted in 1.9 that Rivier and Zlatic (1972 a) have developed a universal curve for lsf scattering in the Al Mn case, which gave a finite resistivity at $T = 0$ and a temperature dependent resistivity initially proportional to $(1 - A T^2)$, then as $(1 - B T)$ and finally as $(- C \log T)$. In a subsequent paper (1972 b) they argue that the lsf dynamics must be essentially the same in Rh Fe as in Al Mn. Whereas in Rh Fe the lsf occur in the d band and the scattering of conduction electrons increases as the lsf excitation increases, in Al Mn the lsf occur in a virtual bound state. A conduction electron must first occupy the extra d orbital before lsf scattering may take place. Since the phase shift due to the first process is $\pi/2$ the effect of the lsf can only be to decrease the resistivity from its zero temperature resonance scattering value. Thus the sign of the temperature dependence of the resistivity of Al Mn is the reverse of that of Rh Fe and other lsf systems in which resonances are absent. According to Rivier and Zlatic the resistivity of Rh Fe should increase as T^2 until $0.14 T_{sf}$ (T_{sf} is the spin fluctuation temperature on this model), then as T in agreement with Kaiser and Doniach. At $T > T_{sf}$ however the resistivity is predicted to be proportional to $\log T$ (as Kondo originally suggested for incorrect reasons). The results of this thesis are compared with these predictions both for Rh Fe and for (V-Cr) Fe alloys in which resonances are present.

CHAPTER 2

APPARATUS AND EXPERIMENTAL METHODS

2.1 Cryogenic apparatus: the ^3He cryostat

The major part of the experimental work of this project was carried out in a cryostat which was designed to allow the accurate calibration of resistance thermometers against the vapour pressure scales of ^3He and ^4He . Such measurements cover the range 0.5 K to 5.2 K with a precision above 1 K of ± 0.3 mK, but by applying heat to the thermometer block and using a calibrated resistance thermometer, measurements may be made at higher temperatures; alloy sample resistances were commonly measured up to 40 K though the experimental accuracy diminishes with increasing temperature.

The low temperature enclosure shown in fig 2.1 is about 10 cm in diameter and 30 cm long. It is immersed in a reservoir of liquid helium which is contained in a 13 cm internal diameter stainless steel liquid nitrogen shielded dewar. Certain important features of the cryostat are listed below.

(i) The stainless steel vacuum can is bolted to the flange with an indium 'O' ring seal and during the measurements the interior is continually pumped by an oil diffusion pump to a pressure of less than 10^{-4} mm Hg.

(ii) The vapour pressure block is made of silver and contains a combined ^4He cooling bath and vapour pressure bulb of 60 cc volume, a ^3He cooling bath of 13 cc and a separate 6 cc ^3He vapour pressure bulb for which high purity ^3He is required. The block is supported from the vacuum flange by the thin walled stainless steel tubes which provide access to the helium baths.

(iii) At the centre of the silver block there is a space for a closely fitting cylindrical copper thermometer block of 30 mm dia and

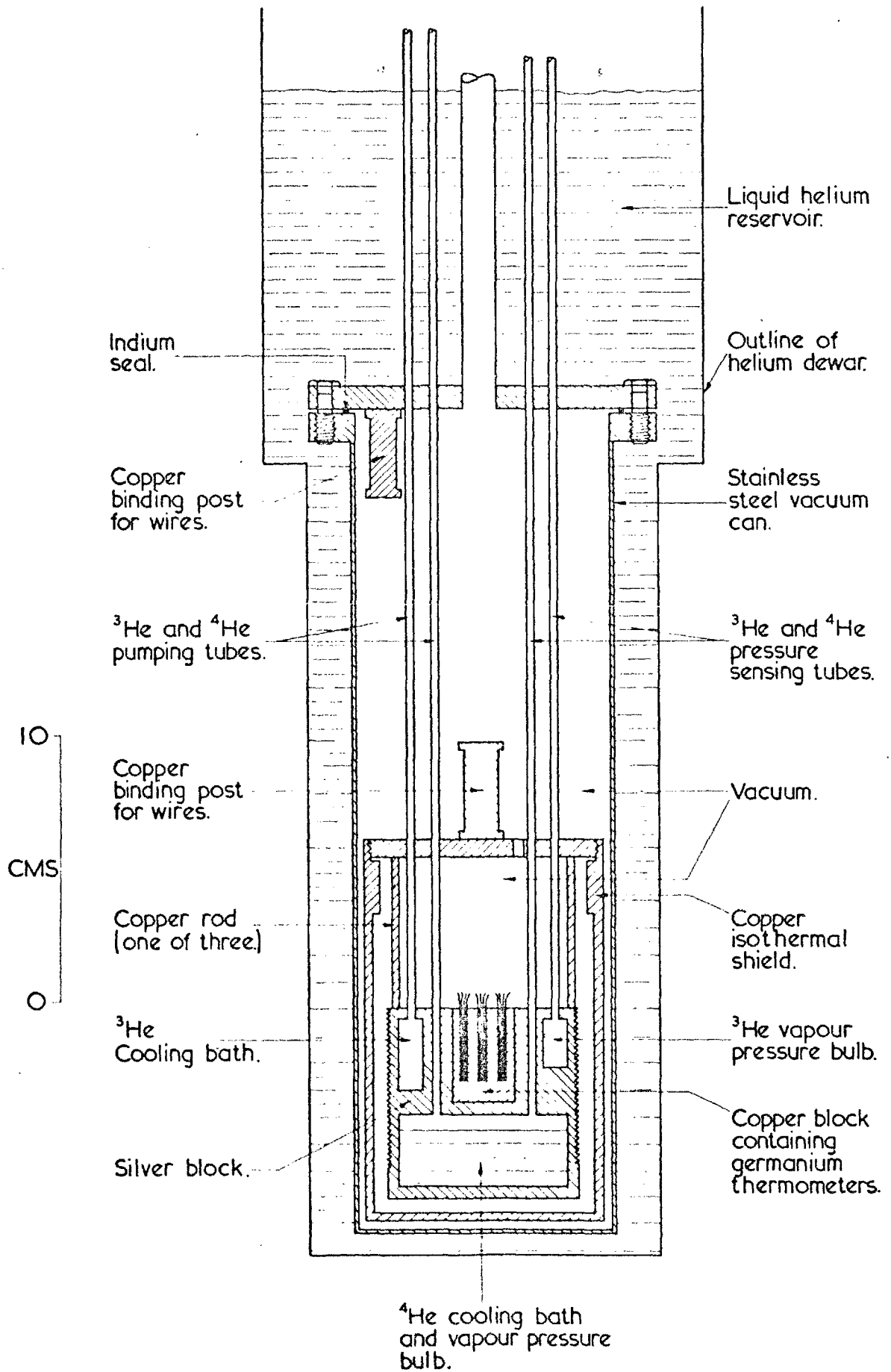


Figure 2.1. The ^3He cryostat

35 mm length. Holes are drilled into it to accommodate capsule type resistance thermometers of various diameters (usually 3' to 5 mm) and it is removable so that holes may be drilled as required. Apiezon 'N' grease is used to increase the thermal contact between the thermometers and the copper and the silver blocks. Contact is further increased by the thermal contraction of the silver which over a length of 30 mm is greater than that of copper by ~ 0.02 mm.

(iv) The copper isothermal shield consists of a can screwed to the copper plate which in turn is attached to the silver block by three 3 mm copper rods. To avoid problems arising from the differential contraction between copper and stainless steel, the tubes are not soldered at this point. To facilitate the evacuation of the interior there are six 10 mm holes in the upper part of the shield can.

(v) Tubes of diameter greater than 5 mm include radiation traps at 4.2 K and the axes of smaller tubes are displaced slightly so that room temperature radiation and gas molecules are unable to penetrate the working space directly. The thermometers and alloy samples are further protected from radiation and residual gas flow by the isothermal shield.

(vi) Electrical leads, 36 in number and of 0.12 mm diameter copper wire, are insulated with 'bicelflux' which has the convenient property of melting at soldering temperatures. They are admitted to the working space by two 5 mm diameter tubes (not shown in fig 2.1) and are vacuum sealed at room temperature using glass-to-metal seals whose pins are small bore tubes. The wires are unbroken through the tubes and 'araldite' vacuum seals were found to be completely reliable. The alternative of using seals at the vacuum flange in liquid helium has the advantage that the wires are more efficiently cooled, but the disadvantage that such seals (often made with 'stycast' or other araldite based material) are more likely to leak and thereby introduce

helium into the vacuum.

On entering the low temperature enclosure, the wires are bound at 4.2 K by winding them round a copper post which is in contact with liquid helium and varnishing them to it. In order that the heat conducted to the thermometer block should not be excessive, a length of ~40 cm of finer copper wire (0.08 mm) is inserted in each lead between this binding post and one on the isothermal shield (originally constantan wire was used, but at high currents the heat generated was significant and thermoelectric effects were also observed). The thermal anchoring of the wires is completed by binding and varnishing them in grooves cut in the silver block, before connections are made to the thermometers or the samples.

2.2 Operation of the ^3He cryostat

After precooling with liquid nitrogen, and with helium gas at ~1 mm Hg pressure in the inner vacuum, the cryostat may be cooled to 4.2 K in about 1 hour for the loss of about 5 litres of liquid helium. The exchange gas is then pumped away and the reservoir is filled to a level of liquid about 15 cm above the vacuum flange. The ^4He bath in the silver block is filled by opening a needle valve (not shown in fig 2.1) situated about 3 cm above the flange. With the valve once more closed, the temperature of the block is reduced by pumping the ^4He bath to 3 K or lower so that the liquid helium occupying the tubes is removed. The first measurements were usually made at 1.8 K. The temperature is determined by measuring the vapour pressure and is controlled to within 1 mK using a manostat connected in the pumping line (though a stability of ~0.1 mK can be achieved for about 10 minutes by manual control of a needle valve). At the conclusion of each point the temperature is raised by applying heat to the block and adjusting the control pressure of the manostat. In this way measurements of resistance and temperature may be made over the range 1.8 K to 4.2 K. The measurements at the

normal boiling point are complicated by the necessity of pressurising the liquid helium reservoir to about 10 cm Hg overpressure, thereby raising its temperature by about 0.01 K to eliminate the possibility of condensation of helium vapour inside the tubes.

While the temperature may be measured using ^4He vapour pressures down to 1.5 K with reduced accuracy, it is preferable though less convenient to use ^3He vapour pressure scale below 1.8 K. The procedure is as follows. The ^4He is pumped to about 1 K. The ordinary grade ^3He (10 litres at NTP) is bled from storage cylinders at a pressure of 20 cm Hg below 1 atmosphere, through a charcoal purifier at 77 K which absorbs air, into the cryostat where it condenses in the pumping bath. The higher purity ^3He (2.5 litres at NTP) is similarly condensed into the vapour pressure bulb. On the completion of these processes (15 minutes) the cylinders are shut and heat is applied to evaporate the ^4He which is continually pumped. This is necessary because of the substantial specific heat of ^4He and the heat leak caused by superfluid film flow. When the boiling is accomplished the temperature rises sharply to about 1.5 K and the controlled heat source cuts off. The temperature of the block may now be adjusted by pumping the ^3He through a manually operated needle valve, and temperature control of ± 0.1 mK may be achieved for a few minutes, down to the lowest temperature obtainable, 0.55 K. This is relatively high for a ^3He cryostat and is due mainly to the conduction of heat through the copper leads. The quantity of ^3He available allows at least 6 hours operation without recharging, and at the conclusion of the measurements ^4He is admitted to the block, the remaining ^3He boils off and is collected in the cylinders.

2.3 Temperature measurement, 0.5 K to 4.2 K

Using the vapour pressure scales of ^3He or ^4He , the measurement of temperature is transformed into the measurement of the pressure existing in equilibrium at the surface of the pure liquid. The relationship

between the two quantities is thermodynamically expressed by an integration of the Clausius-Clapeyron equation, but the calculation of one from the other requires the knowledge of further quantities, such as the latent heat at the absolute zero, L_0 , the molar entropy and volume of liquid, the virial coefficients and the gas constant. It is simpler to base a scale on a direct comparison of vapour pressure measurements with temperatures derived from gas thermometry. The currently accepted ^4He vapour pressure scale (Brickwedde et al. 1960), dating from 1958 and called T_{58} , was derived in this way and uses the thermodynamic relation mainly to extend the range to low temperatures where only L_0 need be assigned a value. The T_{58} scale runs from 0.5 K ($P_{58} = 1.6 \times 10^{-5}$ mm Hg) to the critical point 5.22 K ($P_{58} = 1744$ mm Hg). Subsequently ^3He vapour pressures were calibrated against T_{58} in the range 0.9 K to 3.3 K (Sydoriak et al. 1964) and again using the thermodynamic equation at lower temperatures, the ^3He vapour pressure scale, T_{62} , was derived, covering the range 0.2 K ($P_{62} = 1.2 \times 10^{-5}$ mm Hg) to the critical point 3.3 K ($P_{62} = 873$ mm Hg). In the present cryostat the two vapour pressure scales have been found to agree to ± 0.2 mK in the range 1.8 K to 2.9 K, and there is no evidence to suggest that they disagree outside these limits. However there is considerable evidence from gas thermometry (Berry 1972), acoustic thermometry (Plumb and Cataland 1966, Colclough 1972) and magnetic thermometry (Cetas and Swenson 1972) that the normal boiling point of ^4He on the T_{58} scale is 8 to 10 mK too low, but that the deviations from thermodynamic temperature diminish with decreasing temperature.

Although mercury columns have traditionally been used to measure pressures in vapour pressure thermometry, manometers and McLeod gauges are difficult to operate and it was decided in this work to use commercially available instruments operating on other principles.

In a pressure balance (piston gauge or dead weight tester) a well machined cylinder fits closely over a matched piston with its axis

vertical (fig 2.2). The cylinder may be made to 'float' if the excess pressure inside it exerts an upthrust which exactly balances its weight. This condition is best observed if the cylinder is spun about its axis to eliminate static friction, and the instrument contains a mechanism for achieving rotation. If the space above the assembly is evacuated, the balancing pressure has a well-defined value given by the cylinder weight divided by an 'effective' area whose value may be determined by direct measurement of the cross sectional areas of the cylinder and the piston. The uncertainty of about 20 ppm in the value of the effective area is the major contributor to the uncertainty in the balancing pressure, though this is observed to be stable to a few ppm. By loading the cylinder with calibrated weights the balancing pressure may be varied from the minimum, with the cylinder alone, to the maximum allowed by space. In the present work the range 15 to 1000 mm Hg was obtained using two piston and cylinder assemblies of different cross sectional areas.

The pressure balance is a convenient and accurate primary pressure standard. However it is not by itself suitable for vapour pressure measurements as it is not a continuously reading device. The actual methods used to measure the pressures are different for each isotope of helium, and these are discussed below, together with some practical difficulties.

(i) ^3He vapour pressure measurements

The ^3He vapour pressure sensing tube terminates at a diaphragm maintained at 40 °C whose displacement is detected by a capacitance measurement thereby giving a measure of small pressure differences. The gauge used, the 'Baratron' gauge, was manufactured by MKS Instruments Inc. and has a range of ± 10 mm Hg with a resolution of 10^{-4} mm Hg. The reading is given directly in pressure, and after a calibration correction has been applied (normally not more than 0.01 mm Hg) the gauge may be read with an accuracy of about 0.05%. To make a measurement of pressure

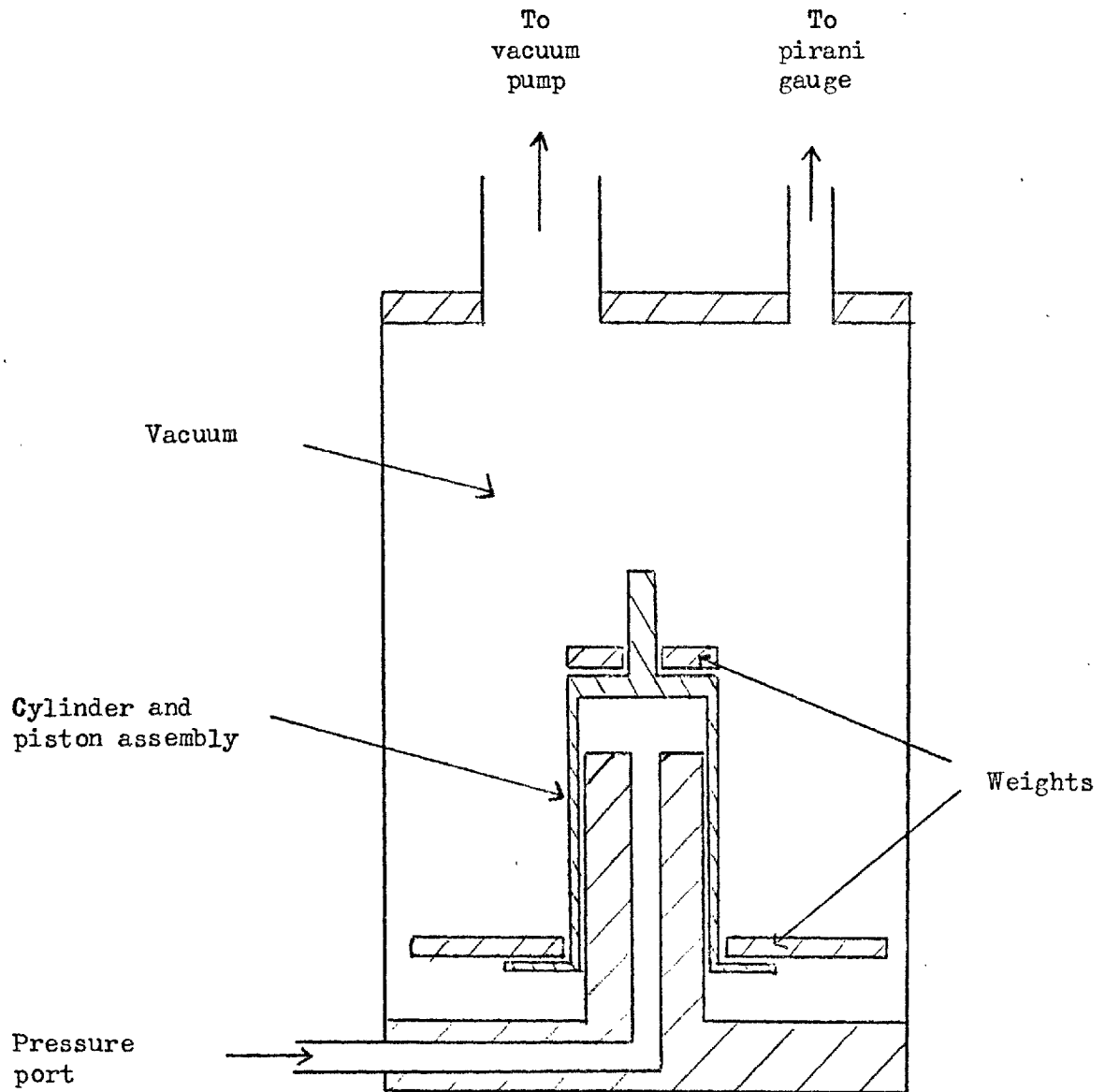


Fig 2.2. Schematic diagram of the pressure balance

below 10 mm Hg the reference side of the diaphragm is evacuated, but for higher pressures a reference pressure P_R is generated using the pressure balance. Vapour pressures in the range $(P_R - 10)$ to $(P_R + 10)$ mm Hg may now be measured, and the 20 mm Hg span is wide enough to allow this method to be used up to the boiling point, with appropriately chosen reference pressures.

Corrections which must be applied to ^3He vapour pressure measurements are firstly those due to the hydrostatic head of the vapour. The magnitude of this effect is estimated to be 0.4 mK at the boiling point, and less at lower pressures. Secondly ^4He contamination introduces an error of about 0.13 mK and 0.05 mK at 3.2 K and 1 K respectively, for the high purity ^3He which contains about 0.02% ^4He . Thirdly the thermomolecular pressure difference between the cold and the warm ends of the sensing tube becomes significant at low pressures. This may roughly be calculated using the Weber-Schmidt equation which for a tube of 5 mm diameter gives corrections of about 1 mK and 8 mK at 0.65 K and 0.5 K respectively.

(ii) ^4He vapour pressure measurements

There is no separate vapour pressure bulb for ^4He ; the 2 mm sensing tube is used to measure the vapour pressure of the same liquid that is pumped to provide cooling. This is because below the lambda point, 2.172 K, the liquid is superfluid and a thin film creeps up the walls of the vessel and the tubes until it reaches a point where it can evaporate. The vapour then causes a pressure gradient and a flow of gas down to the liquid where the cycle is completed by condensation. The effect of the pressure gradient by itself is small (Sydoriak and Sherman 1964) but the consequent flow of gas and condensation introduces a heat flow into the liquid. In a vapour pressure bulb of normal dimensions the Kapitza thermal resistance between the liquid and the container is such that this heat influx causes the temperature of the liquid to rise several

millikelvins higher than that of the container (Montgomery and Matthew 1966). As the vapour pressure liquid is also the coolant in the present arrangement, the block cannot be maintained at equilibrium at a lower temperature than the liquid. A disadvantage of the present design is that temperature and pressure gradients may be established as a result of the continuous pumping of the helium. However, in tests above the λ -point in which the ^3He pumping bath was used as a ^4He vapour pressure bulb, it was found that errors due to this cause were less than 0.1 mK.

A correction must be applied to a ^4He vapour pressure measurement for the hydrostatic effect of the column of gas, which is calculated to be 0.6 mK at the normal boiling point. No correction is necessary for impurities since the ^3He content of naturally occurring helium is negligible, and the thermomolecular effect is also negligible at pressures encountered above 1.5 K.

The instrument used for the measurement of ^4He vapour pressures is a sensitive 'quartz spiral' bourdon-type gauge manufactured by the Texas Instrument Corporation. The angular deflection of the closed end of the spiralled quartz tube under a differential pressure is detected by reflecting a beam of light from a mirror as in a galvanometer. Using a photocell and a high ratio gearing system the 100° deflection which is produced by a pressure difference of 1 atmosphere is subdivided into 300,000 divisions, each equivalent to 2.5×10^{-3} mm Hg. The gauge must be calibrated before use and this is achieved using the pressure balance. In practice the full resolution of the gauge is not available as the calibration does not remain sufficiently constant even over short periods. Furthermore after the pressure in the gauge is altered the reading is observed to drift slowly as a result of a 'relaxation' in the quartz. On returning to the initial pressure a shift of approximately the same magnitude as the relaxation is found, and this decays toward the original

reading with a similar time constant. As the required accuracy for vapour pressure measurements, equivalent to 0.1 mK, is only about 100 ppm, however, the gauge is satisfactory for this purpose provided that calibration checks are made and differential pressures are not maintained for periods of hours.

2.4 Temperature control and measurement above 4.2 K

It has already been mentioned that if the helium in the silver block is boiled away and heat is applied, then measurements of thermometer or alloy sample resistances may be made at temperatures above 4.2 K. The temperature is measured using a rhodium-iron thermometer, manufactured by H Tinsley and Co Ltd (see chapter 4), which is calibrated against the vapour pressure scales below 4.2 K, against the IPTS-68 between 13.8 K and 90 K and against a germanium thermometer in the range 4.2 K to 20 K. An eighth order polynomial fit to 17 data points in the range 1.8 K to 40 K gave a standard error in the residuals ($T_{\text{fit}} - T_{\text{data}}$) of 0.007 K which arose mainly from the use of three different temperature scales. A full range fit from 1.8 K to 90 K gave unacceptably large residuals but a fourth order polynomial fit in the range 34 K to 80 K gave a standard error of 0.03 K and was used for temperatures above 40 K.

The temperature controller used is similar to one described by Compton (1970). It consists of a Wheatstone bridge with an 'Allen Bradley' carbon resistor (of about 100 ohms at room temperature and 9000 ohms at 4.2 K) in one of the arms as the temperature sensor situated at the silver block, and a resistance box in another arm. The temperature of control is selected by setting the appropriate value on the resistance box. The out-of-balance signal from the bridge is amplified and passed to a psd and d.c. power amplifier, and if the temperature is too low, to the 100 ohm constantan wire heater wound on the base of the silver block. At equilibrium the amplified out-of-balance signal provides just enough current in the heater to maintain the block at the desired temperature. Typical

dissipations are 9 mW and 30 mW at 20 K and 40 K respectively, and control is achieved after a few minutes at 20 K, and after about 20 minutes at 40 K.

In this way it has been found possible to compare resistance thermometers with an accuracy of better than 1 mK at 20 K. At higher temperatures it may be predicted that thermal gradients within the block will become significant and the possibility of errors will increase. The resistance thermometers are all situated closely together in the copper block and thermal gradient effects are therefore minimised, but the samples are attached near the base of one of the copper rods connecting the silver block with the isothermal shield (see section 2.5). A calculation shows that if at 40 K all the 30 mW heat input flows up the three copper rods (in fact some flows up the wires and the tubes) then the temperature difference between the block and the shield is ~ 0.07 K. Thus the samples are probably about 0.01 to 0.02 K below the temperature of the block and an error in the measurement results. The estimated uncertainty in the measurement of the temperature of the samples therefore rises from ± 0.003 K below 5.2 K, to ± 0.01 K between 5.2 K and 20 K, ± 0.03 K from 20 K to 40 K and ± 0.05 K at higher temperatures. While these errors are large in comparison with, for example, the accuracy with which thermometers may be calibrated, the errors in the measurement of the sample resistances make a larger contribution to the overall uncertainty in the resistance-temperature characteristics; ie, because the slope dR/dT is small, a relatively large error in temperature may be tolerated.

2.5 Resistance measurement

In a precision resistance thermometer the sensitive element is enclosed in a strain free manner in a vacuum-tight helium filled capsule. Heat transfer to and from the element is by conduction through the gas and along the electrical leads. To ensure good thermal contact with the body whose temperature is to be measured, the capsule is greased and inserted into a hole in the body and the leads are bound and varnished to it. The body should ideally be isolated from its surroundings, but as this is rarely possible, the immediate surroundings should be maintained at a temperature close to that of the body. In the present cryostat this is achieved by

heat conduction along the three copper rods since at helium temperatures the thermal diffusivity of copper is such that only small temperature gradients may exist along their lengths and the isothermal shield rapidly follows changes in the temperature of the block. This method is preferred to the use of exchange gas, partly because the isothermal shield would have to be vacuum tight and low temperature wire seals would be required, and partly because the flow of heat would be less controlled. In particular heat would flow directly from the shield to the thermometers and their leads and this is undesirable.

For unencapsulated resistivity samples, however, measurement in a vacuum is a disadvantage. The electrical leads must be relied on for the achievement of equilibrium and the level of Joule heating which may be tolerated is relatively small. To increase the thermal contact in the present work, the samples were electrically connected to the block and the cryostat was used as one of the current leads. The samples, which were up to 1.9 mm in diameter and mostly less than 40 mm long, were mounted in the following manner. Four 0.15 mm platinum wires were spot welded to the sample to provide one current and one potential lead at each end. One current lead was soldered to a 0.7 mm copper wire which was permanently soldered near the base of one of the 3 mm copper rods. The remaining three connections were made to the cryostat leads as usual. The copper wire was long enough to attach up to six samples at once and insulation between samples was made with sellotape. Where possible, self heating effect tests were carried out and the current was adjusted to render the effect negligible. The dissipation in a sample was usually about 10^{-6} watts.

When the resistance of rhodium-iron wires were measured a different mounting technique was used. A bobbin was constructed, 2 cm in diameter and 4 cm long, on which the wires were wound, using cigarette paper and varnish for electrical insulation and thermal contact. At the base of

the bobbin there was a 2 BA thread enabling it to be screwed into the copper thermometer block. Heating effect tests showed that a dissipation of 10^{-6} watts did not give rise to temperature errors greater than 1 mK in the range 0.5 K to 20 K.

The resistance measurements were all made by standard four terminal d.c. potentiometric methods, as follows. A constant current is passed through the sample and a standard coil of similar resistance in series with it, and the potential difference across each is measured using the potentiometer. The thermal e.m.f.s. which are always present are allowed for by making a second set of measurements with the direction of the sample current and potentiometer supply reversed. The polarity of the thermal e.m.f.s. is thus reversed relative to the potentiometer reading and the thermal-free values of the potential differences are obtained from an average of the 'forward' and 'reverse' readings. The ratio of the potential differences across the sample and the standard coil gives the ratio of the resistances and hence the sample resistance may be calculated. As ratios are taken, the potentiometer need not be standardised to read absolute volts, but an error may be incurred if the instrument is uncalibrated, that is if the ratios of the voltages developed by successive dials differ from their nominal values by unknown amounts. The requirements are more stringent for the higher voltage dials, but if small changes in sample resistances are to be observed, calibration errors in the more significant places are negligible as they only contribute systematic errors. Some calibration errors may be detected by setting the voltage to the same nominal value in two different ways, but for precise measurement a full calibration is required.

In the earlier experiments of this work a Diesselhorst potentiometer was used. Five decades were available, the lowest of which gave steps of 100 nV which could be interpolated to ± 10 nV using a galvanometer amplifier and a secondary galvanometer. Latterly a seven decade Tinsley

'stabaumatic' potentiometer became available and was used to resolve voltages to ± 1 nV. A calibration of the potentiometer showed that the two least significant dials were accurate to 2 nV, the third could give an error of 4 nV while the fourth was correct to 1 nV. In most cases the setting of the third dial was unchanged for a given sample during a run, and therefore the effect of the calibration was small.

The improved resolution of the measurements obtained by the use of the stabaumatic potentiometer was only fully achieved after two other improvements were made. Firstly the bank of five accumulators which were used as the source of the current was replaced by a stabilised current supply, and secondly much greater care was taken to reduce thermal e.m.f.s., particularly those arising at room temperature where thermopowers are large. In spite of this thermal e.m.f.s. of 500 nV were experienced though there was no evidence that drifts in their values introduced errors into the measurements. This was deduced by inspection of the readings which were taken in the following manner. The current was switched to flow through the sample to be measured and the corresponding potential leads were selected for connection to the potentiometer. Readings of sample voltage were taken in the forward and reverse current directions, followed by readings, forward and reverse, of the potential across a 0.01 ohm standard resistance whose value and temperature coefficient were known. Finally readings of sample voltage in both current directions were repeated. A complete set of six readings was accomplished in about 5 minutes, after which the next sample was selected. By taking four readings of sample voltage the random error in the average is reduced by a factor of two. It was also possible to check the consistency of the two pairs of readings and if necessary to repeat them. Also, the difference between the 'forward' and 'reverse' readings gives twice the thermal e.m.f., and it is possible to detect changes in its value during the measurements. In practice it was found that the scatter in the resistance data was equivalent to a

scatter of about ± 3 nV in the measurement of the sample voltage. This is shown in figs 5.6 and 5.9 in which vertical lines indicate the errors in resistivity equivalent to errors of 5 or 10 nV in the sample voltage.

2.6 Sample preparation

The majority of the samples prepared for this work were vanadium and vanadium-chromium based alloys whose resistivities are discussed in chapter 5. The argon arc furnace used has been described by Stone (1971) and was operated by him. The preparation of a sample proceeded roughly as follows. The required quantities of the pure metals were grouped together on the water cooled copper hearth. In an atmosphere of argon at a pressure of 40 cm Hg, a 60 amp arc from a tungsten electrode directed at the material was sufficient to cause melting. After cooling, the button so formed (of about 1 gram) was turned over and re-melted twice to ensure its homogeneity. It was then manoeuvred to lie over the entrance to a cylindrical cavity in a mould (of 1.5 to 3 mm in diameter and 40 mm long) whose axis was vertical. When the sample was once more melted the sudden evacuation of the cavity caused the alloy to be sucked into the mould and to solidify in the cylindrical shape. The cast sample was retrieved by opening the mould which was of split construction, cut through the axis of the cavity.

The casting operation is a matter of skill and timing. Clearly the button must be fully molten before suction, but if this is delayed too long the melt may feed into the mould under gravity and solidify prematurely, so blocking the passage of the remaining alloy. These difficulties are reflected in the quality of the samples produced. A minority were regular solid cylinders over a substantial part of their lengths, many were partly hollow or irregular cylinders, while some were slivers. From the point of view of the measurements the latter were preferable since the resistances per unit length were greater than they would otherwise have

been and therefore smaller anomalies in the resistivities could be resolved. However in determining the absolute magnitude of such a resistivity an effective cross sectional area must be deduced by devious means, no direct measurement being feasible.*

After casting, the vanadium alloys containing up to 10% of impurity were drawn or rolled to increase the resistance. At a chromium content of 40% or more however, the alloys were too easily fractured for such treatment to be practical and the measurements were made on the samples as cast. The smallest diameter mould which gave satisfactory suction was found to be about 1.9 mm in diameter, though some attempts using a 1.5 mm mould were successful. The dimensions of the individual samples, together with other data, are given in tables 5.1 and 5.2.

Of the rhodium alloys only a sample containing 0.4% iron and a sample of pure rhodium wire suction cast. Samples of Rh Co, Rh Mn and Rh Cr whose resistivities are reported in chapter 3 were all available from previous studies by Mozumder (1967). Most of the Rh Fe samples were obtained in

*

A measurement of sample volume (eg by mass and density measurements) is also inadequate since

$$V = \int_0^l A(x) dx$$

whereas $R = \rho \int_0^l \frac{dx}{A(x)}$

In both cases the integral is taken over the length of the sample between the potential contacts and $A(x)$ is the cross sectional area at a distance x from zero. Only if $A(x)$ is constant over the length may its value determined from a volume measurement be used to calculate the resistivity.

the form of wires from Engelhard Industries Ltd and the method of preparation is discussed in chapter 4.

2.7 The dilution refrigerator

The measurement of the resistivities of rhodium-iron alloys at temperatures below 0.5 K was an important part of the project from both the physical and thermometric points of view. The dilution refrigerator used for this purpose was of NPL design and largely of NPL construction. A major feature of the design was that in an effort to achieve high circulation rates and powerful refrigeration for long periods, the cryostat and the refrigeration unit were large. In the event the circulation rate was not as high as had been hoped, but a temperature of 0.02 K was reached and the cooling powers were comparable with those of Wheatley et al. (1968), and was for example 100 ergs/sec at 0.08 K.

As its construction was not part of this project, the refrigerator will not be described in detail except for the mixing chamber where the cooling is achieved. This is drawn life size in fig 2.3. It is constructed in an epoxy material, Epibond 100-A, for two main reasons. Firstly the magnetic thermometer used would induce eddy currents in a metallic container. Secondly the parts of the mixing chamber may be glued together and yet withstand a vacuum and remain impermeable to superfluid helium. Thus the lid is stuck to the chamber, the inlet and outlet tubes (2 mm diameter cupro-nickel) are glued in place and the electrical connections to the interior are made via 12 bare 0.2 mm copper wires which are glued in holes in the lid and the body of the chamber.

The cerium magnesium nitrate (CMN) powder used in the magnetic thermometry is contained in a 2.5 cm right cylinder at the base of the mixing chamber and is therefore permeated by superfluid helium and is in good thermal contact with the dilute phase of the mixture. Its susceptibility was measured using a mutual inductance bridge operating at 12 Hz. The primary coil was formed by 60 turns of superconducting wire and

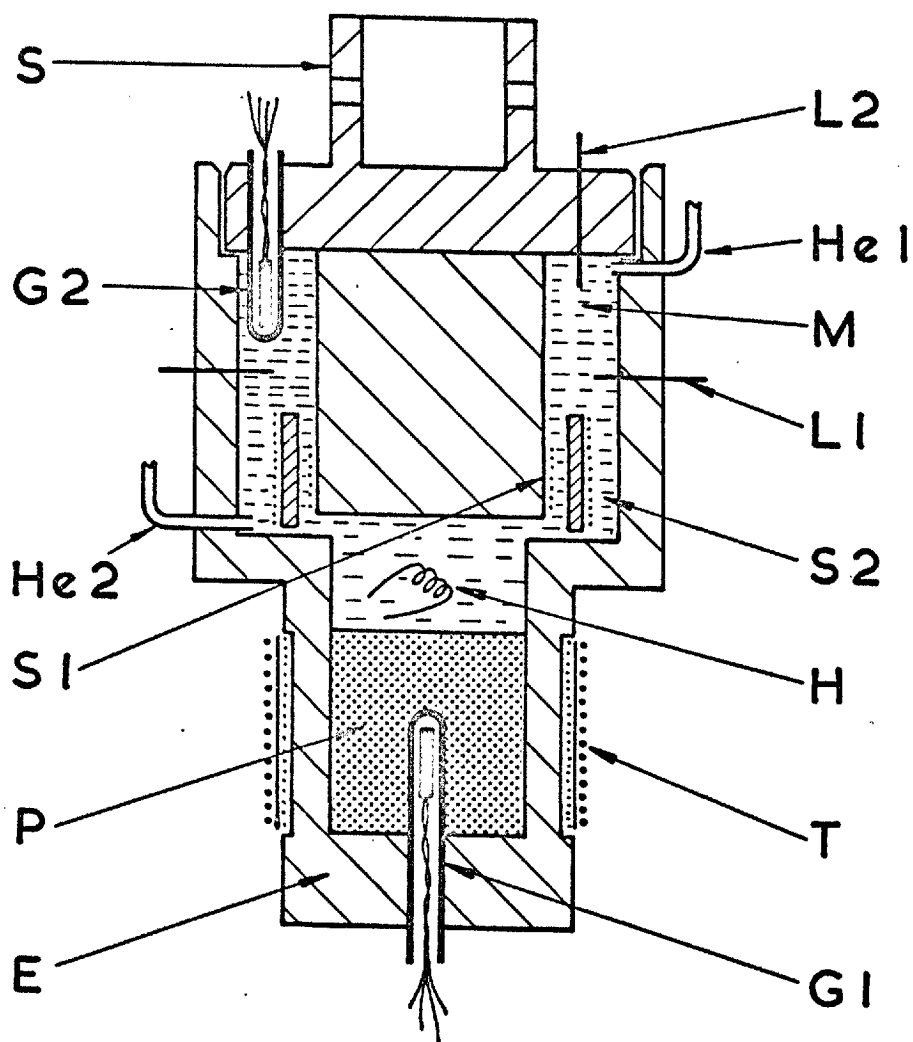


Fig 2.3. The mixing chamber of the dilution refrigerator, life size
 Code: E, epoxy container; M, ^3He - ^4He mixture; He1, ^3He inlet tube; He2, ^3He outlet tube; P, CMN powder; T, superconducting primary and copper secondary coils of the magnetic thermometer; G1 and G2, germanium thermometers inserted in copper sleeves; H, electrical heater; L1, one of six electrical lead-throughs; L2, as for L1; S, chamber support; S1 and S2, samples of rhodium-iron wire.

the secondary consisted of 600 turns of 0.03 mm copper wire. A pair of vacuum cored dummy coils of nominally the same construction was suspended 10 cm below the mixing chamber and the secondary coils of each set formed two arms of the bridge. Balance was achieved by adjustment of an inductive divider which constituted the third and fourth arms. The bridge reading (ie the setting of the inductive divider) varied linearly with the susceptibility of the CMN and therefore with the inverse of the temperature. The thermometer was first calibrated in the range 0.5 K to 4.2 K using calibrated germanium thermometers and the best straight line through a plot of bridge reading versus $1/T$ was extrapolated mathematically to give the magnetic temperature scale whose accuracy was approximately 1%.

As the CMN powder was situated in the dilute phase of the mixture it was important that the rhodium-iron wires whose resistivities were to be measured should be mounted near the base of the chamber. The 0.5% Fe sample was mounted on a nylon rod of diameter 30 mm which occupied the central space (and allowed a simple method of varying the volume of the mixture from run to run). The second sample of 0.06% Fe was wound on an epoxy former of 46 mm diameter which was glued to the base of the chamber and in which holes were drilled to allow the flow of liquid. In one experiment the superconducting transitions of some vanadium-chromium alloys were investigated but these were mounted externally to the chamber. Thermal contact with the liquid was achieved through a 3 mm copper rod which entered the mixing chamber through the lid to which it was glued. About 12 fine copper wires were brazed to the rod to increase the contact area, though at the lowest temperature (30 mK in this experiment) the temperature difference between the liquid and the samples was probably not negligible.

Operation of the refrigerator proceeded as follows. The helium mixture was condensed at 1.2 K and slowly passed through a capillary constriction to cool the dilution unit below 4 K. During this process the CMN susceptibility was calibrated against the germanium thermometer.

When the condensation was completed, further cooling was achieved by pumping on the still, which was maintained at ~ 0.65 K, and after about 1 hour phase separation occurred in the heat exchanger system. When sufficient ^3He had been circulated the phase boundary was forced into the mixing chamber and rapid cooling ensued. Calibration of the salt pill was continued down to 0.5 K, below which the temperature was deduced from the extrapolation of the calibration data. The rate of cooling decreased as the temperature fell and though 0.1 K was reached after pumping for 8 hours, it required a further 8 hours to cool to 0.03 K. The cooling eventually ceased at 0.025 K and the temperature was subsequently adjusted by the application of heat to the mixture. The cooling power as a function of temperature was calculated from the measured heat inputs and was found to be reproducible. In order to cool below 0.025 K the flow of ^3He returning to the cryostat was halted thereby reducing the heat leak into the mixing chamber. This then cooled rapidly until either the ^3He was exhausted or the still was emptied and evaporation curtailed. In this way the lowest temperature of 0.020 K was reached.

The measurements of resistance were made during the cooling process as this was sufficiently slow not to introduce significant errors below 0.5 K. Thermal gradients are however present above the lambda point of the mixture and during the separation of the phases. Furthermore the initial cooling was very rapid and it was therefore difficult to achieve accurate results above 0.5 K.

CHAPTER 3

RHODIUM BASED ALLOYS

3.1 Introduction

The original results for the resistivity of dilute rhodium-iron alloys (Coles 1964) were outlined in section 1.11. It was found that the impurity resistivity per percent of solute was roughly independent of concentration up to 0.8% and increased rapidly with temperature in the range 1 K to 50 K. The effect of a 14 kGauss magnetic field was to increase the resistivity of a 0.5% alloy by about 2% at 4.2 K and Kohler's rule was apparently obeyed.

Later the susceptibility of Rh Fe was measured and found to be similar to that of Cu Fe at low concentrations. At higher concentrations (3 to 15% Fe) magnetic order was observed (Murani 1969, Murani and Coles 1970) similar in character to that of the spin glass ordering of Cu Mn. The resistivity per impurity atom was found to increase with concentration in this region, though the temperature dependence of the resistivity of the more concentrated alloys is reduced. It is interesting to note that whereas the transition to the spin glass state in Cu Mn is marked by a resistance maximum, Murani found resistance minima in his 11% and 15% samples of Rh Fe.

Elucidation of the Rh Fe phenomenon was also sought from resistivity measurements of alloys of Rh with Cr, Mn, Co and Ni solutes. Mozumder (1967) found a similar though smaller effect in Rh Mn, the other alloys giving normal temperature independent residual resistivities to within the accuracy of the measurements.

In this chapter new results are presented for the resistivities of these samples and small effects in Rh Cr and Rh Co are described. Measurements of the resistivity of Rh Fe made in the dilution refrigerator down to 0.02 K are presented and it is shown that the theories of

Kaiser and Doniach, and Rivier and Zlatić are applicable to this system though an interesting concentration dependence in the scaling temperature is observed. Finally an unexpected effect found at low temperatures is discussed.

3.2 Resistivity of 3 d solutes in rhodium

As it was proposed to develop a rhodium-iron thermometer it was clearly necessary to obtain this alloy in wire form and the difficulties associated with this are discussed in chapter 4. For the present purposes it need only be stated that the determination of the resistivity of a 0.5 atomic % Fe in Rh alloy in the range 0.5 K to 90 K (fig 3.1) was made using about 100 cm of a 0.13 mm diameter Engelhard wire of the batch labelled in chapter 4 'E II'. The calibration of the wire from 4 K to 90 K was made in a cryostat specially designed for the comparison of resistance thermometers (Rusby et al. 1972) using a platinum thermometer above 14 K and a germanium thermometer calibrated against the provisional acoustic scale of the National Bureau of Standards, Washington, in the range 4-14 K. A thermometer using this wire was constructed by winding it on a copper bobbin with varnish insulation, and was used in the helium vapour pressure cryostat (fig 2.1) to measure temperature in the range above 4.2 K until a capsule-type rhodium-iron thermometer became available. The resistance of the thermometer was converted to the resistivity of the wire using its measured dimensions and the resistivity change ($\rho_T - \rho_{4.2}$) was assumed to be reproducible from run to run. $\rho_{4.2}$ was checked during each run and was not found to vary significantly. While this procedure enabled the temperature to be measured to ± 0.02 K near to 4.2 K, at higher temperatures it becomes increasingly inaccurate, probably approaching ± 0.1 K at 20 K, and therefore the thermometer was suitable only as a temporary expedient. Measurements of temperature in the range 0.5 K to 4.2 K were made using the helium vapour pressure scales.

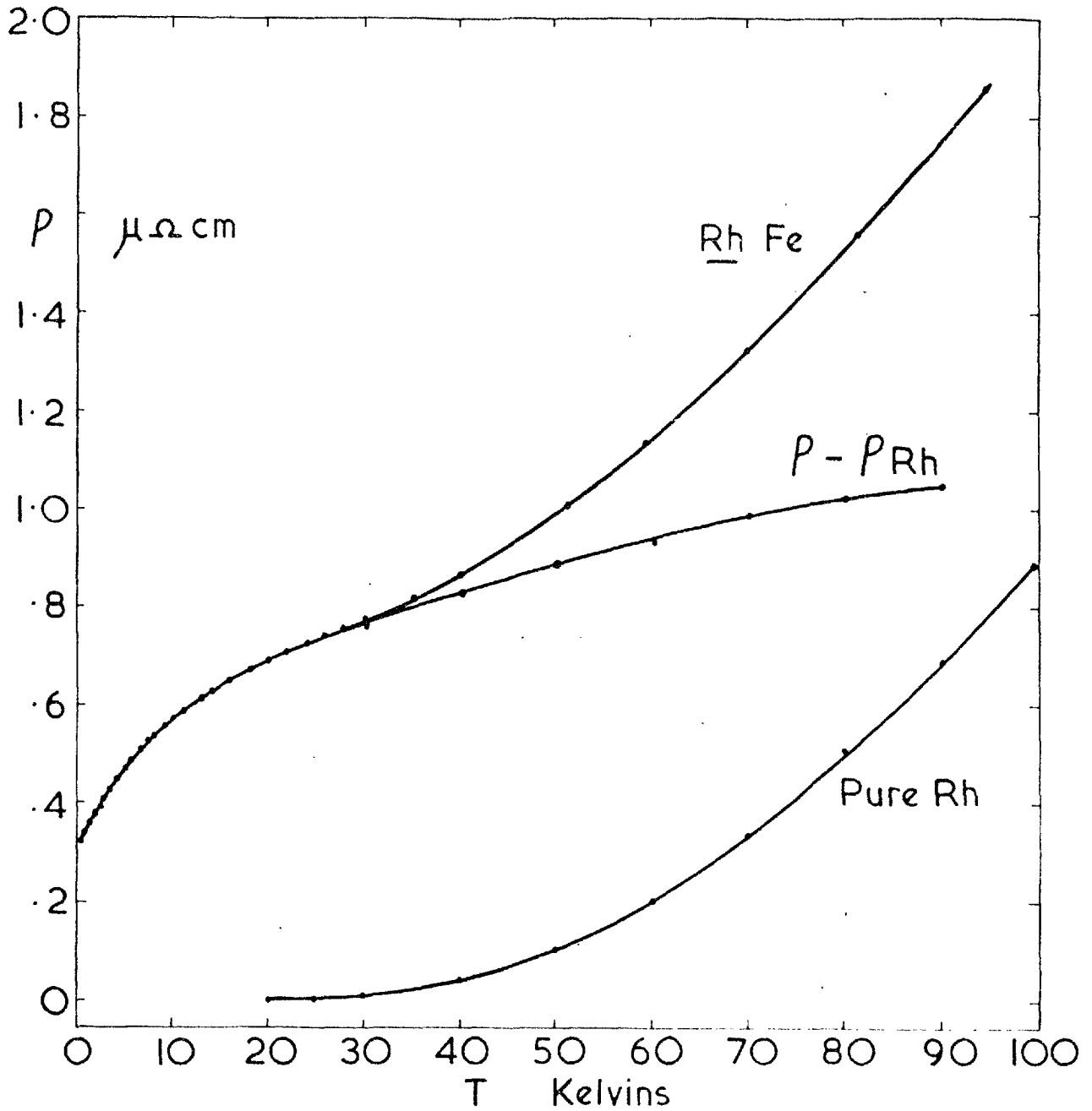


Fig 3.1. The resistivities of the E II Rh - 0.5% Fe alloy, of pure rhodium (from White and Woods 1959), and of Rh - 0.5% Fe after subtraction of the host resistivity.

Samples of Rh Cr, Rh Mn and Rh Co were all available from previous experiments. The Rh Cr, containing nominally 0.5% Cr, was 12.8 mm long and about 1.25 mm in diameter. Its resistance at 4.2 K was about 0.2 m Ω and was measured using a current of 10 mA. The Rh Mn, also nominally a 0.5% alloy, had been drawn down to 0.52 mm diameter and the length between the potential contacts was 7.8 cm. The Rh Co sample, believed to be a 1% alloy, had also been drawn to 0.52 mm diameter and the length between contacts was 9.45 cm. The resistances of these two samples at 4.2 K were about 2.8 m Ω and 1.9 m Ω respectively and the measuring current was 6.5 mA in both cases. A Diesselhorst potentiometer was used to compare the sample voltage with that of the standard resistance.

The results of the resistivity measurements of these samples and the Rh Fe results are plotted from 0.5 K to 50 K in fig 3.2, which is a slightly amended version of a figure published elsewhere (Coles et al. 1971). White and Woods' (1959) values for the ideal resistivity of pure rhodium are also included. The Rh Cr sample had a high residual resistivity which was temperature independent within the experimental accuracy up to 15 K but thereafter fell by about 0.1 $\mu\Omega$ cm to a minimum at about 37 K for reasons which have been discussed by Rivier and Zitkova (1971, see also sections 1.5 and 3.5). The resistivity of Rh Mn was found to be similar in character to that of Rh Fe, though the residual resistivity was larger, and the temperature dependence was smaller. Also in common with the results for Rh Fe, there was no sign of a linear region or a T^2 dependence down to 0.5 K.

The Rh Co sample showed a small temperature dependent increase in resistivity due to the impurity of about 0.04 $\mu\Omega$ cm at 40 K. These results are enlarged in fig 3.3 (note that since the sample was thought to contain 1% Co* the impurity resistivity was divided by 2 for the

* A microprobe analysis subsequently indicated a cobalt concentration of 0.85 atomic %.

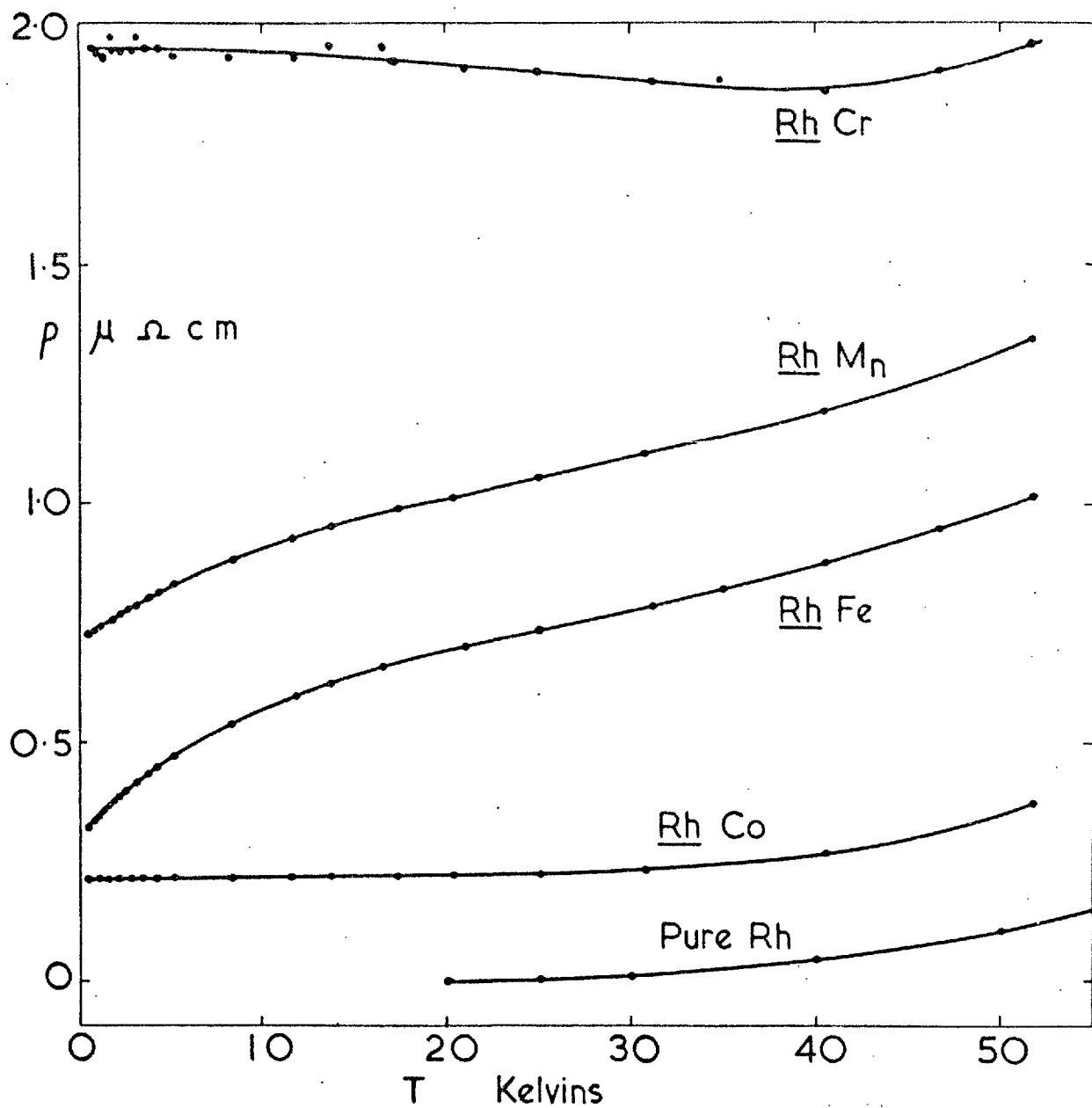


Fig 3.2. The resistivity of rhodium alloyed with about 0.5% Cr, Mn, Fe and Co, and of pure rhodium (from White and Woods 1959)

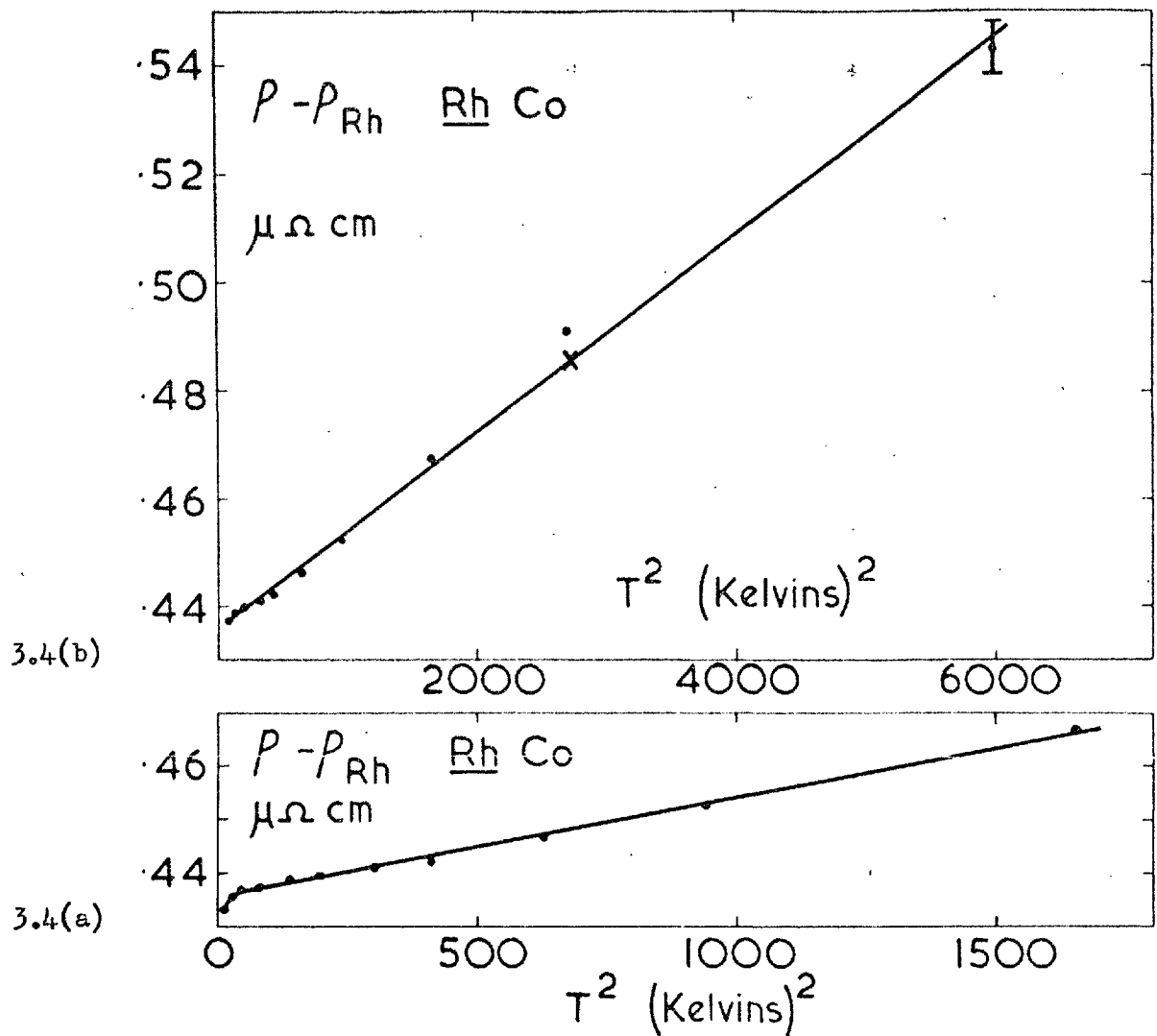


Fig 3.4. The impurity resistivity of Rh - 0.85% Co against T^2
(a) up to 40 K (b) up to 77 K

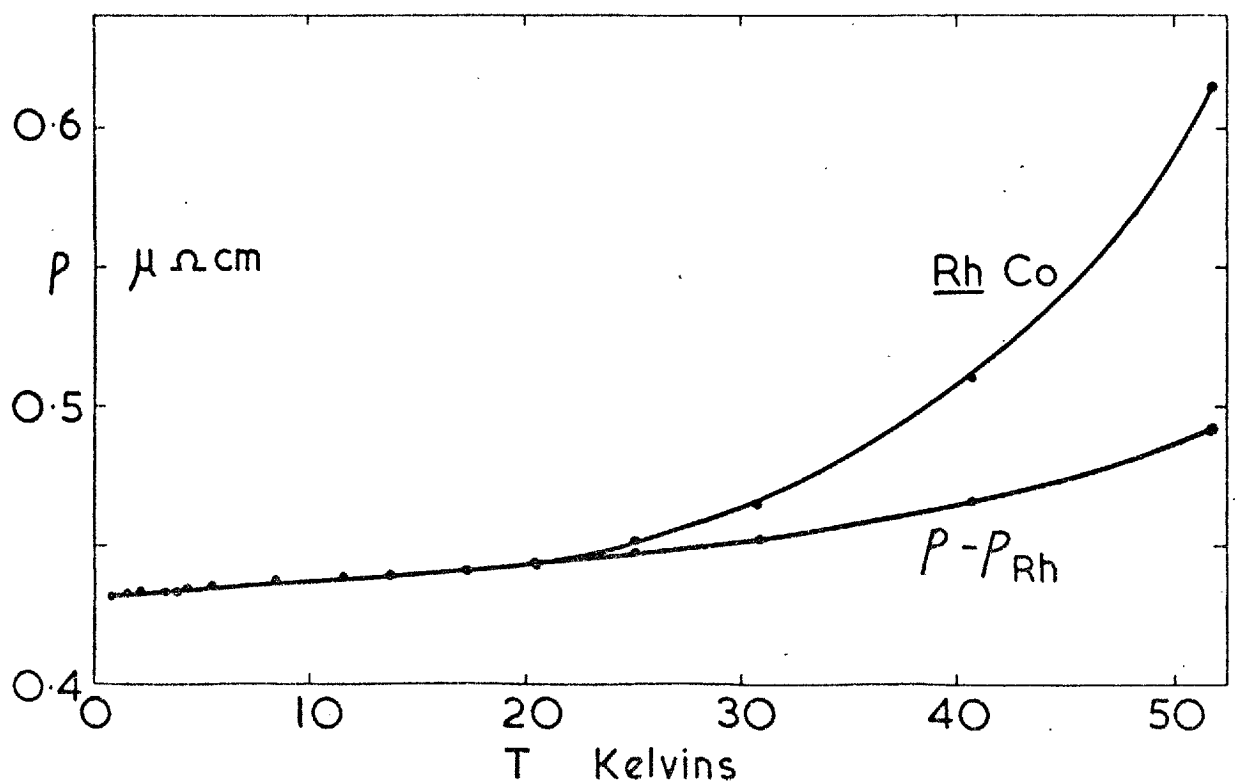


Fig 3.3. The resistivity of Rh - 0.85% Co as a function of temperature

purposes of fig 3.2 only). This increase represents about 8% of the total at 40 K which is too large to ascribe to an error in the factor A/l (cross sectional area to length ratio) for the conversion of resistance to resistivity, which was measured to $\pm 5\%$ (even an 8% error in A/l would not wipe out the observed effect since the residual resistivity would also be affected). The effect at 20 K of $0.01 \mu \Omega \text{ cm}$ is approximately what would be produced by about 200 ppm of iron solute, but the curvature of the characteristic is of the opposite sign for this explanation to be valid. In fact figs 3.4 a and b show that the impurity resistivity may be described by a T^2 law, of coefficient $1.73 \times 10^{-5} \mu \Omega \text{ cm/K}^2$, up to about 77 K, though the room temperature resistivity lies well below this law ($\rho_{300} \sim 5.74 \mu \Omega \text{ cm}$, $\rho_{300} - \rho_{\text{Rh}} \sim 0.96 \mu \Omega \text{ cm}$). Thus it seems that the Kaiser-Doniach theory is applicable to this system, as expected, but with $T_s \sim 400 \text{ K}$ rather than 6 K as was deduced from Houghton and Sarachik's (1969 abstract only) results. The present results are qualitatively similar to those of Nagasawa (1970) which appear to show a transition from a T^2 to a linear dependence at about 70 K, though the magnitude of the impurity resistivity was much larger than is observed here (eg from Nagasawa's data $\rho_{300} - \rho_{\text{Rh}} \sim 1.7 \mu \Omega \text{ cm}$ for a 1% alloy).

A practical detail concerning the measurement of the resistivity of Rh Co at 50 K should be mentioned since the point clearly does not lie on the T^2 line of fig 3.4 b. This is believed to result from the use of use of the crudely constructed rhodium-iron thermometer, which as noted earlier is expected to be less accurate at higher temperatures. At 50 K the resistivity of pure rhodium is increasing at the rate of about $0.01 \mu \Omega \text{ cm/K}$ which is large on the scale of fig 3.4. A temperature error of 0.5 K at 50 K makes little difference to the graphs of ρ vs T (figs 3.2 and 3.3), but the resulting error in $\rho - \rho_{\text{Rh}}$ due to the subtraction of an erroneous value of ρ_{Rh} may be large. The

cross on fig 3.4b shows the result of adding 0.5 K to the temperature of the datum point at 51.9 K. The effect at 40 K is much smaller, and the measurement at 77.4 K was made with the sample immersed in liquid nitrogen and taking an assumed temperature value. The resistivity of pure rhodium at 77.4 K was determined relative to White and Woods' value at 295 K, using a sample prepared in the argon arc furnace at Imperial College and gave a value of $0.472 \pm 0.005 \mu\Omega\text{cm}$ which is consistent with, though more accurate than an interpolated value from White and Woods' table. The uncertainty in the subtraction ($\rho - \rho_{\text{Rh}}$) at this temperature is marked by an error bar in fig 3.4b.

A further feature of the results in fig 3.4a is the fall in resistivity below the T^2 law at temperatures below 5 K. Apart from surmising that this may have been interpreted by Houghton and Sarachik (1969) as a small low temperature 'Rh Fe type' effect, discussion of this observation is postponed until section 3.5.

3.3 Rhodium-iron in detail

Having measured the resistivity of a 0.5% Fe in Rh alloy, it is of interest from the theoretical and thermometric points of view to investigate the concentration dependence of the effect. Accordingly four samples (of batch E III) were prepared by Engelhard Industries, using the same techniques as for E II, as follows: a pure rhodium wire of 0.05 mm diameter and Rh Fe wires of 0.13 mm diameter containing nominally 0.4, 0.5 and 0.6 atomic percent of iron. All the wires were strand annealed for 15 minutes at 1000 °C. 4 platinum leads were flame welded to about 1 metre lengths of each wire and the distances between welds were measured. The wires were then wound on four sections of a single copper bobbin, using cigarette paper insulation and varnish adhesive and thermal contact medium. The bobbin was screwed into the copper thermometer block of the helium vapour pressure cryostat and connections

were soldered to the wires in the usual way. The resistances, and hence the resistivities of the wires were measured from 0.5 K to 20 K at 1 mA current which was found to give negligible heating effects, and the results are plotted in fig 3.5 (note the change in scale for the resistivity of the pure rhodium).

The resistivity of the 0.5% sample is clearly inconsistent both with previous results and with those for the other two alloys. In view of the low resistivity and temperature coefficient it must be concluded that only a small quantity of iron was actually dissolved. Chemical analysis later showed that the full amount of iron was present, and the existence of clusters must be presumed. The original intention of determining the concentration dependence of the resistivity was therefore abandoned and instead the resistivities were used to obtain an 'effective' concentration on the assumption that each iron atom which is dissolved is independent of the others. Then the resistivity $\rho_1(T)$ of alloy 1 with iron concentration C_1 and residual resistivity ρ_1^0 is given by

$$\rho_1 - \rho_{Rh} = \Delta\rho_1 = \rho_1^0 + C_1 F(T)$$

where $F(T)$ gives the temperature dependent resistivity per percent of iron. The relationship between the resistivities of two alloys ρ_1 and ρ_2 at any given temperature is therefore

$$\frac{\rho_1 - \rho_{Rh} - \rho_1^0}{C_1} = F(T) = \frac{\rho_2 - \rho_{Rh} - \rho_2^0}{C_2}$$

and a graph of ρ_1 against ρ_2 (or strictly of $\Delta\rho_1$ against $\Delta\rho_2$ if ρ_{Rh} is significant) should be a straight line, the slope of which is the ratio of the concentrations C_1/C_2 . In fig 3.6 the resistivity of the E III 0.6% sample is plotted against that of the 0.4 and 0.5% samples, giving good straight lines, the deviation at high temperatures arising

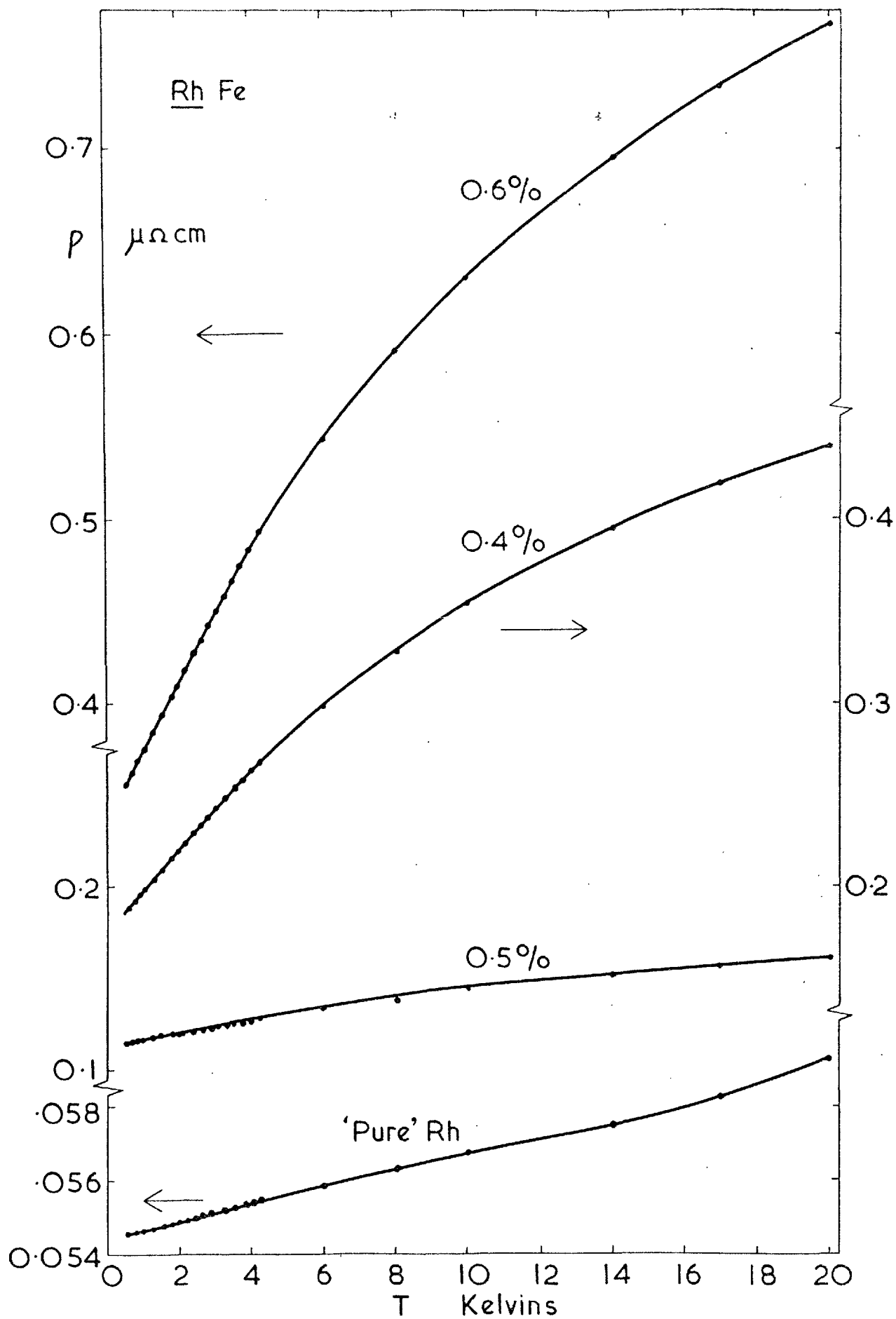


Fig 3.5. The resistivities of E III 'pure' rhodium and Rh Fe with nominally 0.4, 0.5 and 0.6% iron

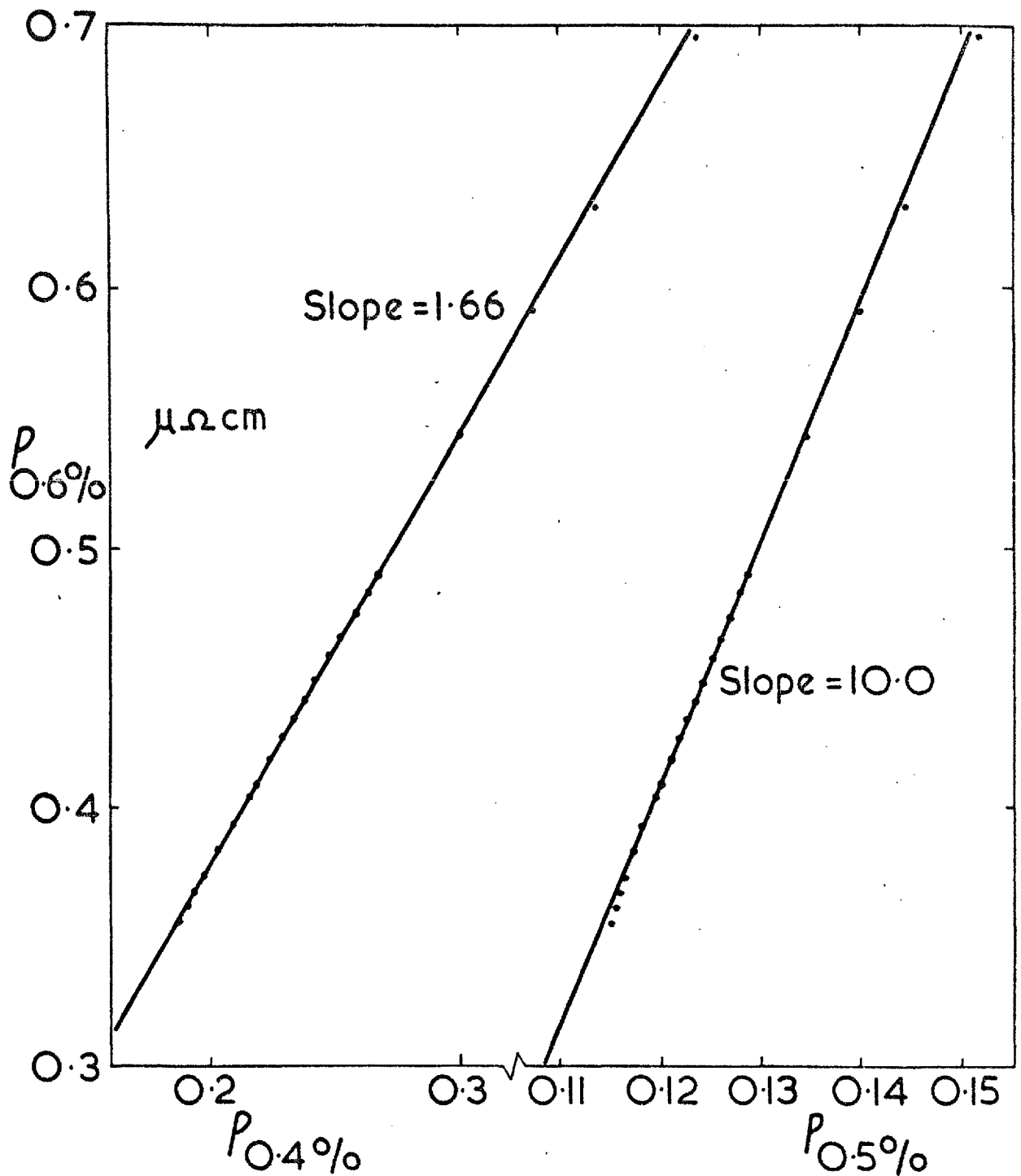


Fig 3.6. Resistivity plots for E III Rh Fe samples, from the slopes of which the ratios of the concentrations were determined

because ρ_{Rh} whose value is uncertain (see below) has not been subtracted. The concentration ratios determined from the slopes of these graphs are 1.66 and 10.0 respectively. Thus by plotting a set of such graphs and assuming the concentration of one alloy, this procedure may be used to calculate the concentrations of other alloys. The following values for the concentrations of the E III alloys and a 0.4% sample prepared at Imperial College were deduced on the assumption that E II contains 0.5% Fe.

E III nominally 0.4%,	deduced concentration 0.35%
" " 0.5%,	" " 0.058%
" " 0.6%,	" " 0.58%
I.C. calculated 0.41%,	" " 0.41%

Support for this set of concentrations may be drawn from the agreement between the deduced concentration for the I.C. sample and the value calculated from the weights of the constituent elements.

The deviation at high temperatures observed in fig 3.6 has been commented on, but there is also an effect at low temperatures in the comparison of the 0.6% and 0.5% samples. The cause of this is shown in fig 3.7 where the resistivity of the 0.5% (from now on referred to as the 0.06% or 600 ppm E III sample) is plotted on an enlarged scale in the helium range, together with that of the E III 'pure' rhodium sample and a 'pure' rhodium sample prepared at Imperial College*. Whereas in the E II 0.5% sample the resistivity (fig 3.1) is decreasing strongly with temperature even at 0.5 K, that of the 600 ppm sample begins to flatten out below 1.8 K. It is also seen that both 'pure' rhodium samples show a temperature dependent resistivity much too large for ideally pure rhodium, and some iron impurity must be presumed to be

* Kindly provided by Dr A Murani.

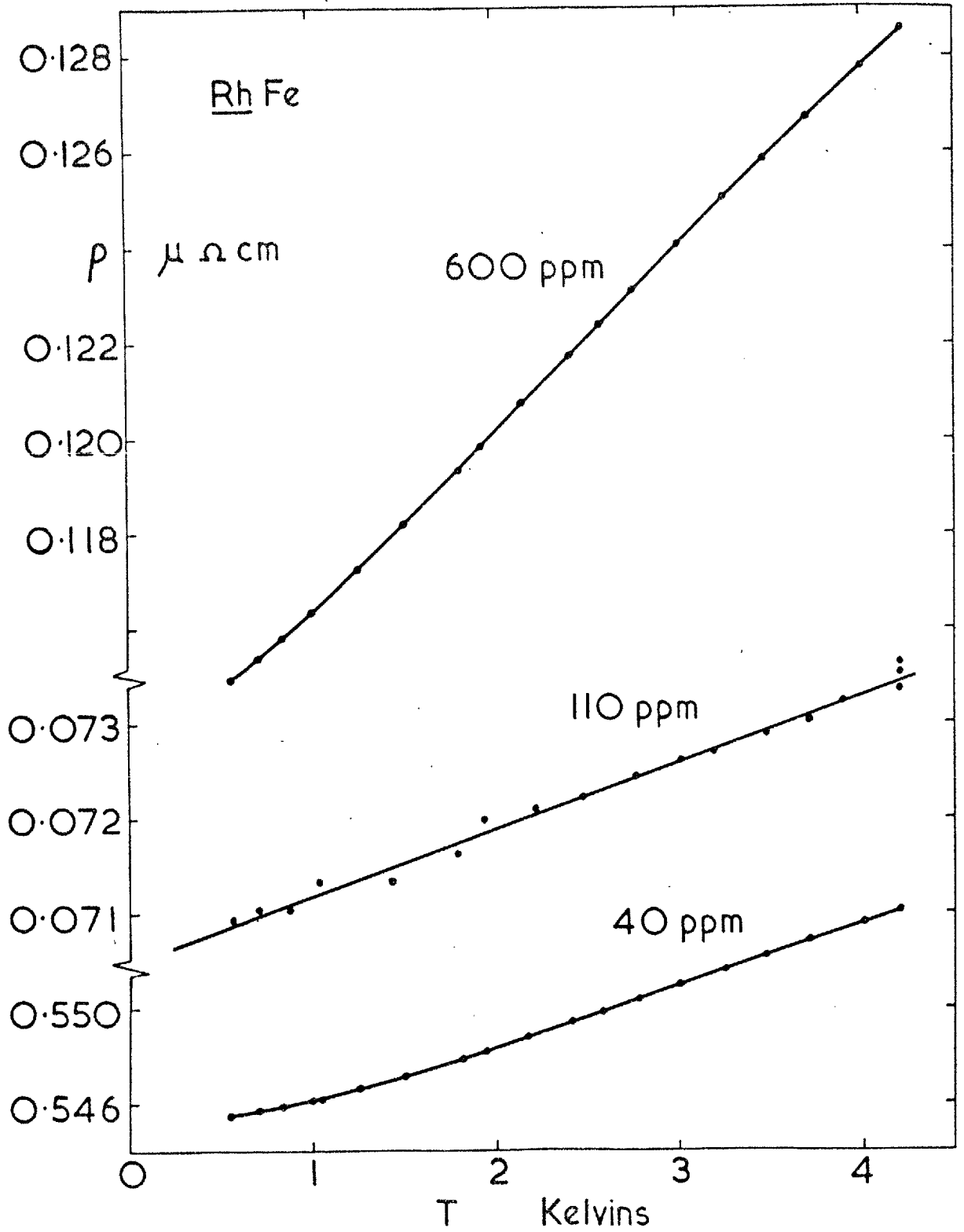


Fig 3.7. The resistivities of dilute samples of Rh Fe, the concentrations of iron as marked

present. By comparing the magnitude of the effects between 1 K and 4.2 K with that in the 600 ppm sample, the iron concentrations were determined as 40 ppm and 110 ppm for the E III and I.C. samples respectively. The shape of the resistivity-temperature curve for the 110 ppm sample was not clearly determined since its resistance was only 0.01 m Ω and the measurements were difficult. The 40 ppm sample however showed a reducing slope below 2.2 K and within the limits of measurement, a linear region extending from 2.0 K to 4.2 K. Thus the Kaiser-Doniach characteristic spin fluctuation temperature T_s , which determines the temperature $T_s/4$ at which the T^2 law gives way to the linear law, would appear to be concentration dependent. The values of $T_s/4$ for the present alloys were roughly estimated to be below 0.5 K in the 0.5% sample, about 0.8 K in the 600 ppm sample and about 1.2 K in the 40 ppm sample. Plots of the resistivities of the 600 and 40 ppm samples against T^2 , however, failed to show a purely quadratic behaviour in either, down to 0.5 K.

3.4 Rhodium-iron below 0.5 K

When the dilution refrigerator became available for experimentation it was naturally used to examine the resistivity of a 0.5% Rh Fe sample below 0.5 K. A length of about 1 metre of 0.05 mm diameter E II wire (of resistance about 2 ohms at 1 K) was wound in a thread cut in a nylon rod of diameter 3 cm and mounted inside the mixing chamber, as described in section 2.7. It was thus situated in the dilute, superfluid phase of the $^3\text{He} - ^4\text{He}$ mixture close to the CMN powder and provided that the self heating was not excessive, the alloy and the magnetic thermometer were at the same temperature. The heating effect was tested at intervals by making measurements at different currents, and the dissipation was reduced so that its effect was less than the resolution of the measurement. The criterion becomes severe

at very low temperatures where the Kapitza boundary resistance is large, and below 0.04 K a current of 20 μ A was used, giving a dissipation of about 10^{-9} watts. In early runs it was possible to make measurements down to only 0.07 K and using a Diesselhorst potentiometer the scatter of the data was such that a linear resistivity - temperature characteristic was deduced (Rusby 1971) in accord with the results of Oliveira and Foner (1971) for a 1% alloy. However when the refrigerator was modified and the 'stabaumatic' potentiometer used the results were extended to 0.02 K with much reduced scatter (fig 3.8 a) and the linear region appeared more as an inflection in the range 0.2 K to 0.3 K either side of which the slope tended to decrease. This suggests that $T_s/4$ is ~ 0.2 K, and is more in agreement with the results of Laborde and Radhakrishna (1971). The data below 0.2 K have the nature of a T^2 dependence, of coefficient $0.126 \mu \Omega \text{ cm/K}^2$, but fig 3.8 b shows that this is only observed over the fairly narrow range 0.05 K to 0.12 K. At lower temperatures still, the resistivity unexpectedly falls below the T^2 law. This fall is a genuine effect as the resistance values repeated on different days and at different measuring currents. Furthermore it is not a particularly small effect: it is larger than the random error in the resistance measurement, and could not reasonably be ascribed to an error in the measurement of temperature.

The second sample whose resistance was measured in the dilution refrigerator was a length of the E III 0.06% wire. The temperature coefficient of this wire is much smaller than that of the 0.5% alloy, and in order to achieve good accuracy without self heating the resistance was made as high as practicable by including a long length of wire. About 3 metres of 0.13 mm diameter wire wound on a threaded former of about 4.6 cm diameter gave a resistance, however, of only 0.3 ohms at 1 K and it was necessary to interpolate the voltage readings to 1 nV. Heating effect tests were not meaningful because of systematic potentio-

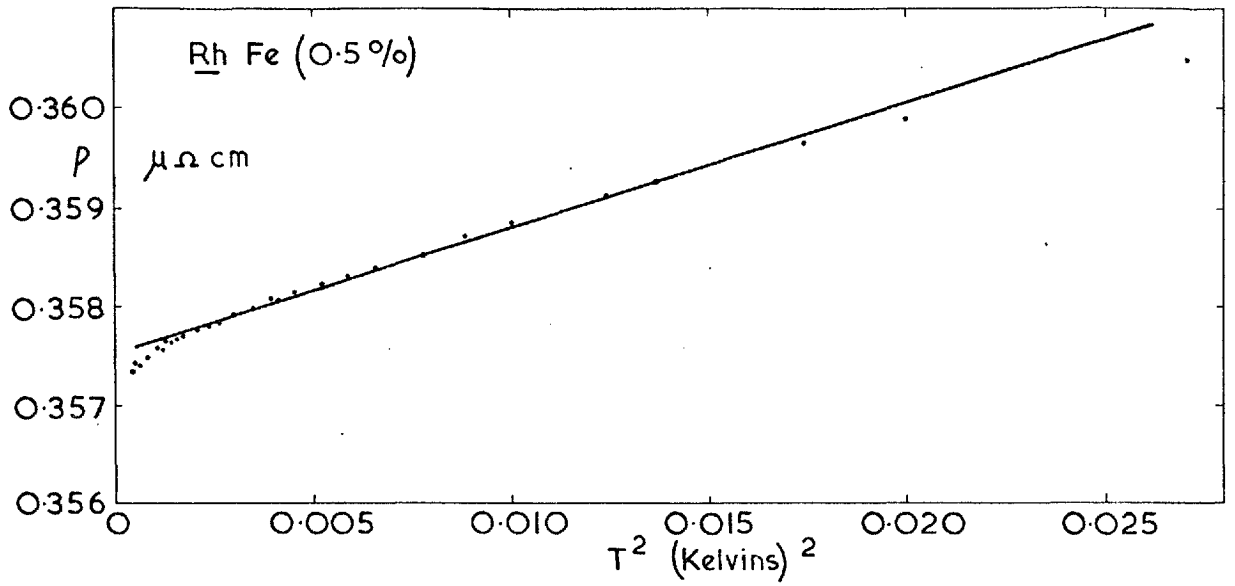


Fig 3.8(b). The resistivity of Rh - 0.5% Fe versus T^2 below 0.16 K

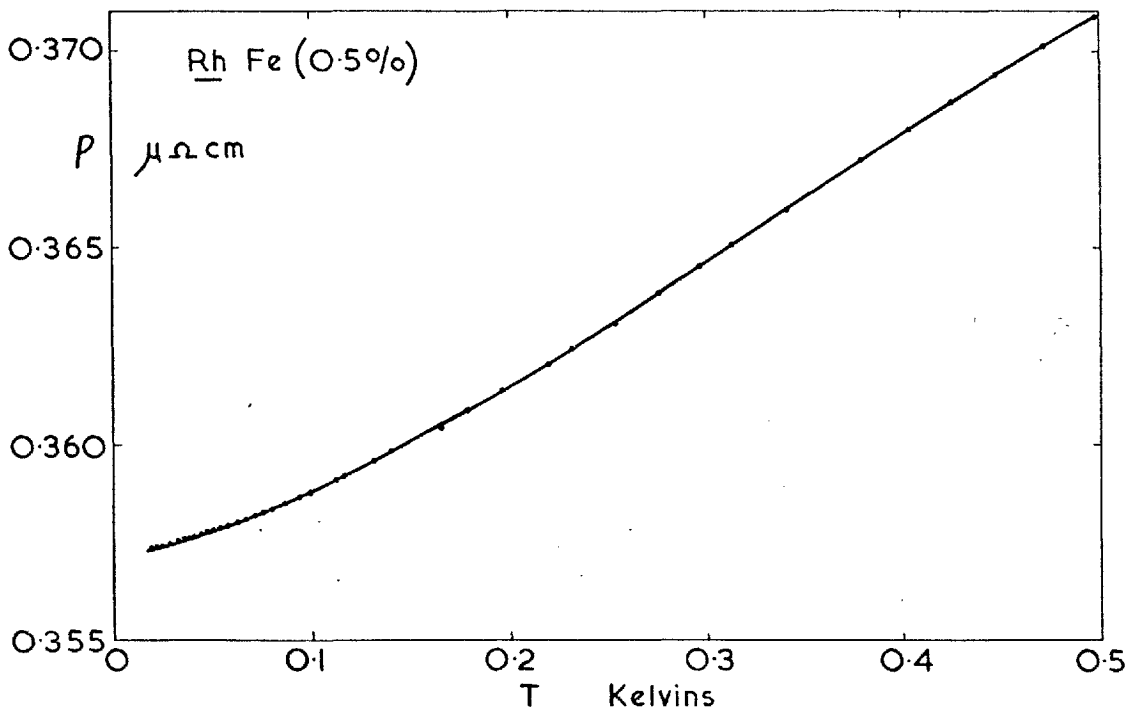


Fig 3.8(a). The resistivity of Rh - 0.5% Fe below 0.5 K

meter errors in the interpolated place. Therefore, below 0.4 K the measurements were all made at 50 μ A giving a dissipation of about 10^{-9} watts as this had been tolerated in the previous experiment under the less favourable conditions of a smaller wire surface area. The results below 0.4 K are plotted against T and T^2 in figs 3.9 a and b. From the latter it may be seen that a T^2 law is obeyed in the region 0.11 K to about 0.4 K, with a coefficient of $4.7 \times 10^{-3} \mu \Omega \text{ cm/K}^2$, but the fall in resistivity which in the 0.5% sample occurred below 0.05 K, was in this alloy observed below 0.11 K. Once again the measurements were repeatable and the effect lay outside the probable error of the experiment.

The dilution refrigerator results are connected with the results in the helium vapour pressure range in fig 3.10 for both the 0.5% and the 0.06% samples and the concentration dependence noted in section 3.3 is clearly visible, the curvatures in the 0.5 to 2 K region being of opposite sign. While $T_g/4$, which marks the change from the T^2 to the linear regime, is about 0.2 K in the 0.5% sample, in the more dilute alloy it is nearer 1 K. Taken with fig 3.7 where the resistivity of the 40 ppm sample suggests that $T_g/4$ is about 1.2 K, these results indicate that iron-iron interactions of the RKKY type, which at higher concentrations lead to 'spin glass' ordering, have the effect at lower concentrations of stabilising the localised spin fluctuations and forcing the characteristic curve to lower temperatures. As a corollary the impurity resistivity per per cent of iron, $\Delta\rho/C$, at a given temperature is expected to increase with concentration, but the fact that plots of ρ_1 vs ρ_2 (fig 3.6) gave good straight lines above $T_g/4$ suggests that $\Delta\rho/C$ is not very different in alloys of up to 0.6% (this is also in agreement with Coles' original results) and that variations in T_g are probably the best indication of interaction effects.

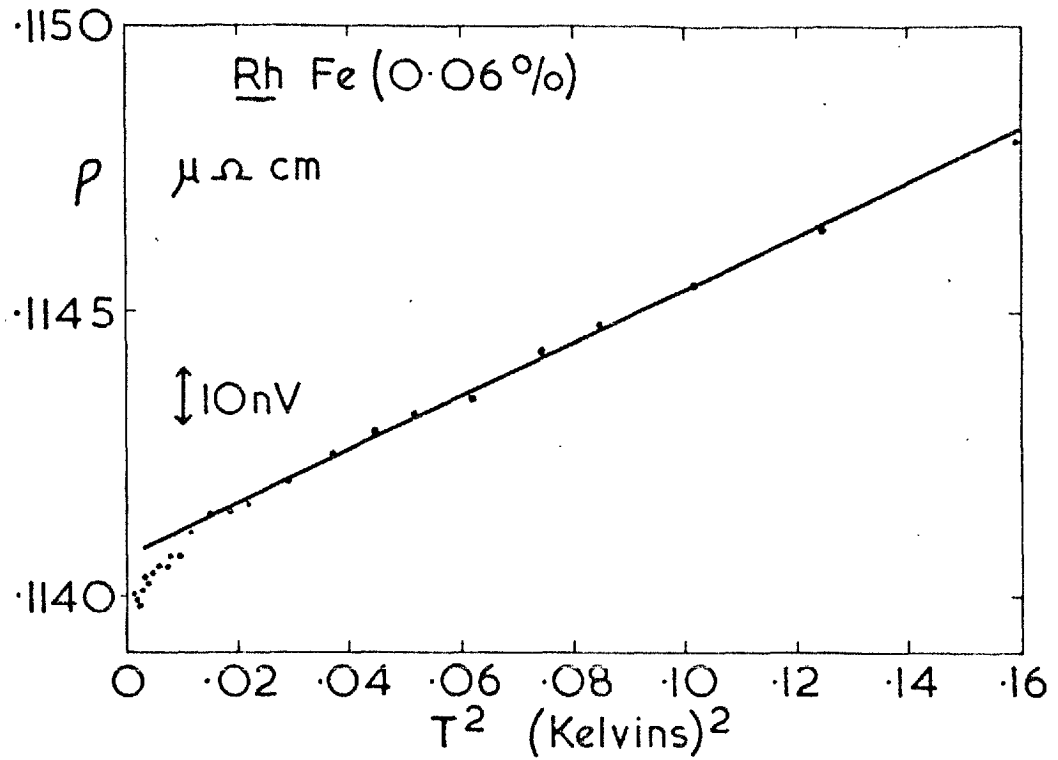


Fig 3.9(b). The resistivity of Rh - 0.06% Fe versus T^2 below 0.4 K

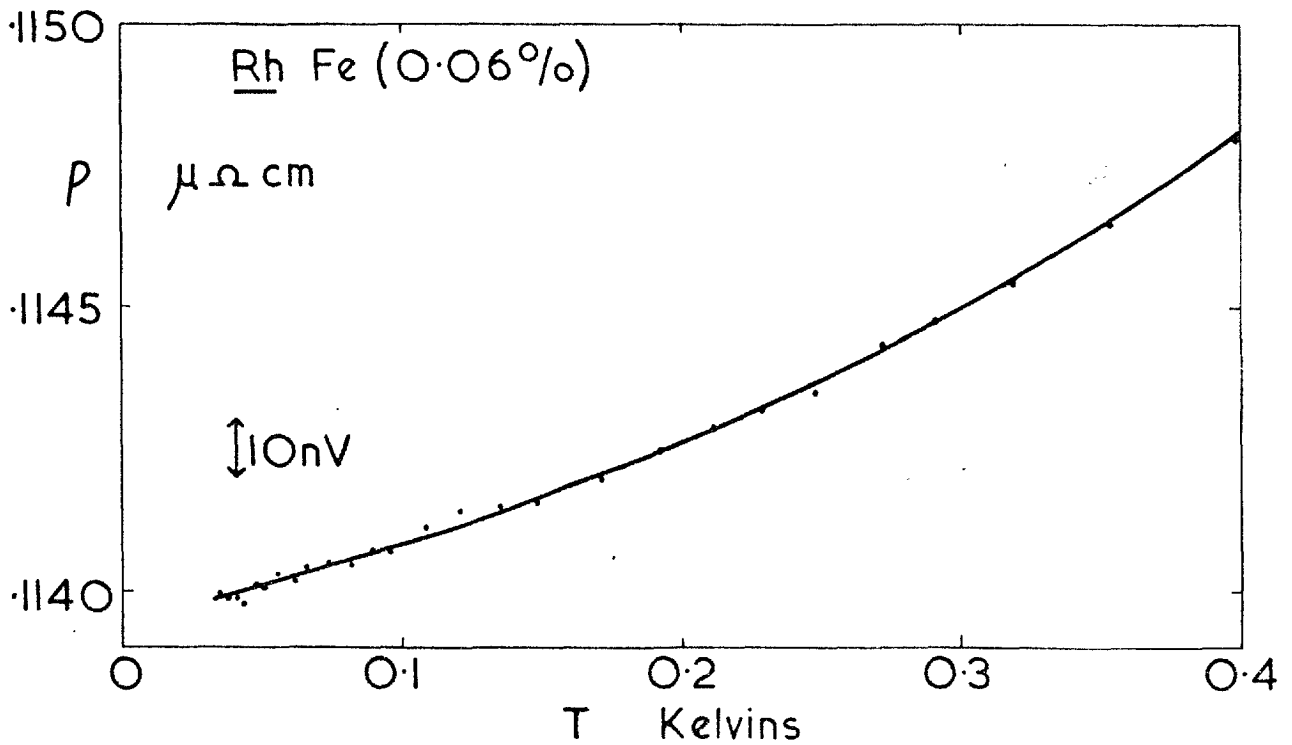


Fig 3.9(a). The resistivity of Rh - 0.06% Fe below 0.4 K. The error in the resistivity equivalent to an error of 10 nV in the sample voltage is indicated

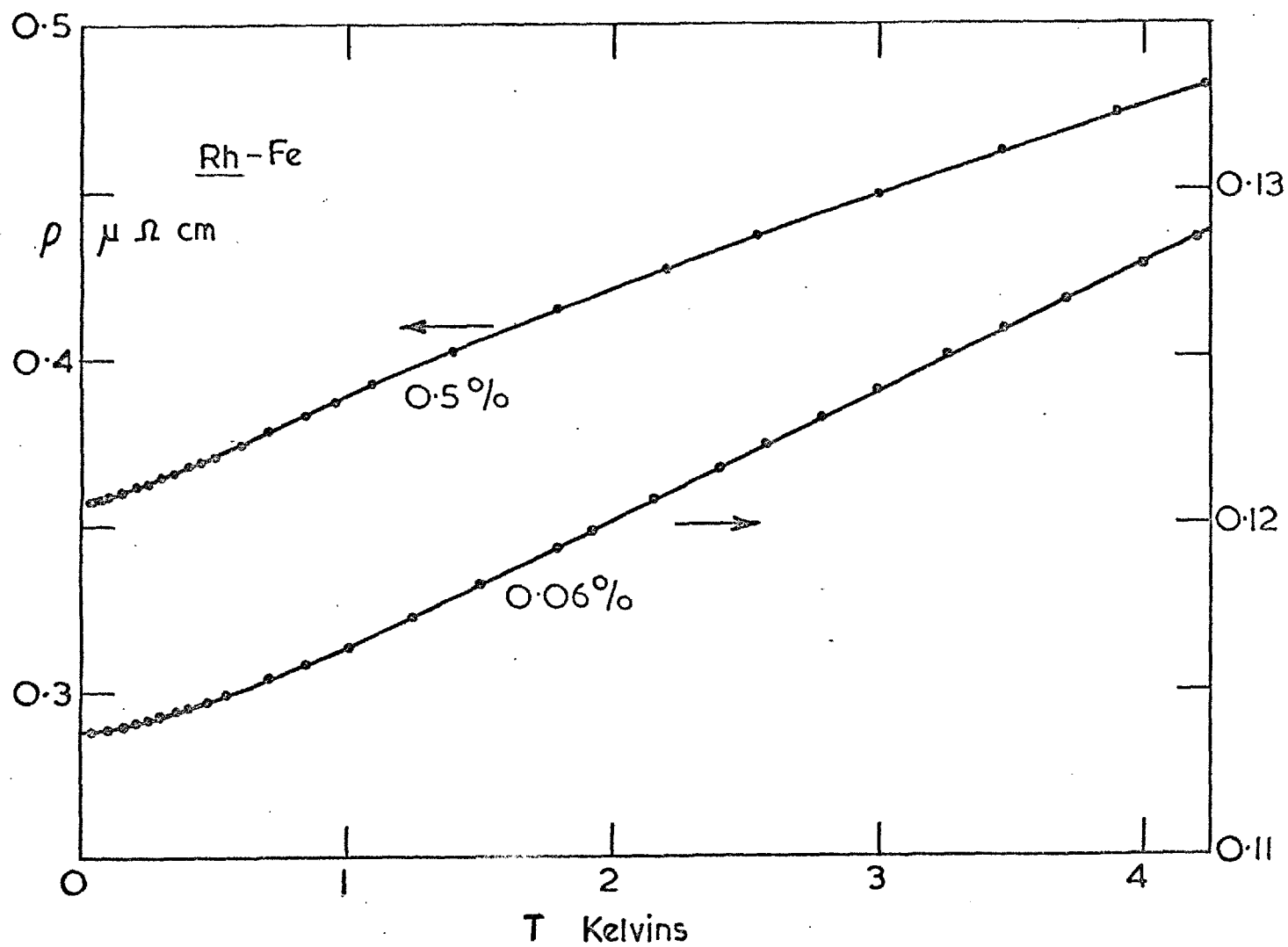


Fig 3.10. The resistivity of Rh Fe containing 0.06% and 0.5% Fe versus temperature from 0.02 K to 4.2 K

3.5 Discussion

The results for the rhodium based alloys have been presented and it is now necessary to examine how well the expectations of the theory have been fulfilled.

As regards the variation of the 3 d solute, no quantitative statement can be made, but certainly the results have found a plausible explanation in Rivier and Zitkova's (1971) transition from a non-resonant (Rh Co) to a resonant (Rh Cr) situation. Co is isoelectronic with Rh and is not expected to cause a large residual resistivity in solution. By analogy with Pd Ni, a T^2 temperature dependence is predicted on the Lederer-Mills or Kaiser-Doniach theories, and the resistivity measurements of figs 3.3 and 3.4 are in accord with this, with $T_s \sim 400$ K. That the spin fluctuation lifetime is short is also borne out by the small temperature dependence of the susceptibility and the absence of magnetic order even in an 11% alloy of Rh Co (Murani and Coles 1970).

Iron in rhodium is more nearly magnetic as indicated by the susceptibility, and the Kaiser-Doniach (and Rivier-Zlatic) characteristic curve is scaled to much lower temperatures, T_s being ~ 4 K. The size of the residual resistivity is larger than in Rh Co and the strong temperature dependence shows that the local enhancement due to iron atoms is large. In Rh Mn the slope $d\rho/dT$ increases as the temperature is lowered to 0.5 K as in Rh Fe. The effect is smaller ($\sim 0.024 \mu\Omega\text{cm/K}$ at 1 K compared with $0.037 \mu\Omega\text{cm/K}$ in Rh Fe) and therefore the enhancement factor would appear to be smaller, but a value of T_s cannot be given as measurements did not extend below 0.5 K or to lower Mn concentrations. Since Rh Cr shows a clear, though weak, resistance minimum, indicative of resonant scattering from a magnetised virtual bound state, it is plausible to suppose that in Rh Mn a complicated balance exists between the collective band and vbs situations which reduces the slope of the

resistivity.

It has recently been shown by Loram et al. (1972) that if some simplifying assumptions concerning phase shifts and charge screening may be made, then the sign of the temperature coefficient of the resistivity due to a transitional impurity in a metal may be roughly predicted from the value of Z , the charge difference between the host and the impurity. Using the Friedel sum rule the scattering cross section was related to the mean square value of the (fluctuating) moment and the impurity resistivity per per cent of solute was calculated in the limits $T \rightarrow 0$ and $T \gg T_s$:-

$$\Delta\rho(0) = 5 C \rho' \sin^2 (\pi Z/10)$$

and
$$\Delta \rho(T \gg T_s) = \Delta \rho(0) + 5 C \rho' \cos (\pi Z/5) \sin^2 (\pi S/5)$$

where S is the high temperature value of the impurity spin and ρ' is the resistivity at the 'unitarity limit' of resonant scattering. These excess resistivities may be calculated as a function of Z and the difference between them determines the total change in resistivity in proceeding from $T = 0$ to $T \gg T_s$ (though not the form of the temperature dependence). The sign of this change is seen to depend on the sign of $\cos (\pi Z/5)$ and is therefore positive for $Z < 5/2$ and negative for $5/2 < Z < 15/2$. Loram et al. were able to show that this model accounts well for the signs and magnitudes of the resistivity changes observed in Pd and Pt alloys, and also after some refinement of the model the present results for rhodium-based alloys were shown to be in reasonable agreement with the predictions.

More stringent comparisons of theory with experiment have been made using the results for the resistivity of dilute Rh Fe as a function of temperature. At the lowest temperatures a T^2 dependence was sought and found, though in the 0.5% sample it was observed only in the relatively short range 0.05 to 0.12 K. In the 0.06% sample the T^2 region was

found to extend up to 0.4 K and the characteristic scaling temperature T_s was evidently reduced in the more concentrated sample by the effects of interactions between iron atoms. At higher temperatures a linear region is predicted, but this appears to be observed only in the dilute limit. Thus in the 40 ppm sample the resistivity is clearly proportional to T between 2.0 K and 4.2 K, and in the 0.06% sample the linear region extends from 1.5 K to 3.0 K. The curvature of the resistivity of the 0.5% sample, however, (fig 3.10) changes sign rather rapidly at 0.5 K and a linear dependence is not clearly established at all.

Rivier and Zlatic (1972 b) predict that above their T_{sf} (~ 12 K in Rh Fe) the resistivity should follow a logarithmic law, and the resistivities of the 40 ppm and 600 ppm samples are plotted against $\log T$ in fig 3.11. In this temperature range however, the resistivity of pure rhodium makes a significant contribution in such dilute alloys, and should be subtracted from the alloy resistivity. Unfortunately, it could not be measured because what is now known as the 40 ppm Rh Fe alloy was itself the purest available sample of rhodium. White and Woods (1959) evidently used purer rhodium (residual resistivity $\sim 0.01 \mu\Omega \text{ cm}$), but their data do not extend to below 20 K and the value of $0.0018 \mu\Omega \text{ cm}$ at that temperature is not accurate to better than 10%. As a rough guide the resistivities of the two dilute alloys at 20 K after subtraction of this value are marked by crosses and the dotted lines make tangents to the curves. There is no indication, however, that these lines represent a good subtraction or that a $\log T$ resistivity is observed up to 20 K.

In more concentrated samples the subtraction is less problematical as ρ_{Rh} represents a smaller proportion of the total resistivity. Furthermore the effect of interactions between impurities is to reduce the characteristic temperature and the logarithmic regime should be observable at lower temperatures. Fig 3.12 shows the resistivities of

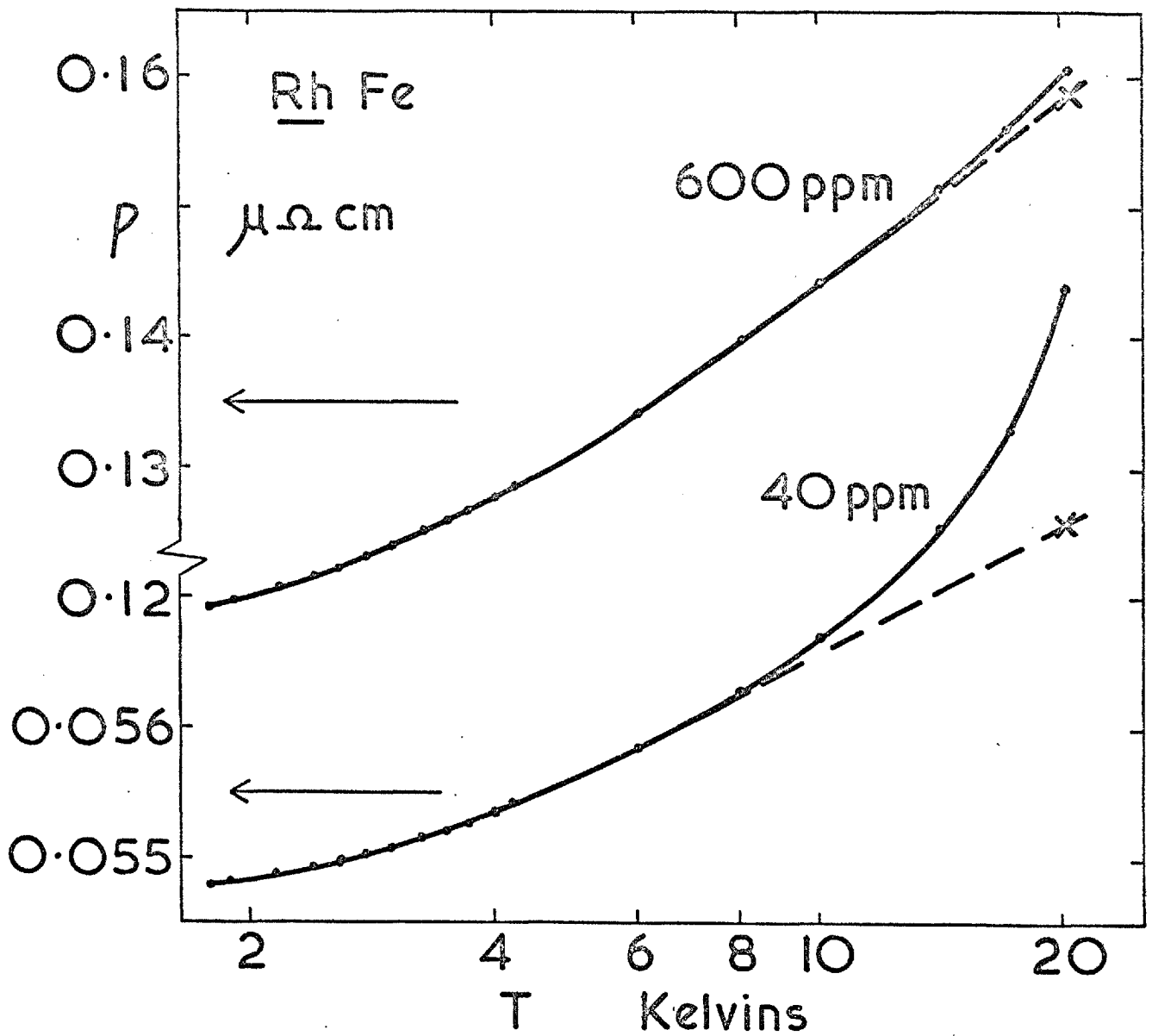


Fig 3.11. The resistivities of Rh Fe containing 40 ppm and 600 ppm (0.06%) iron versus $\log T$

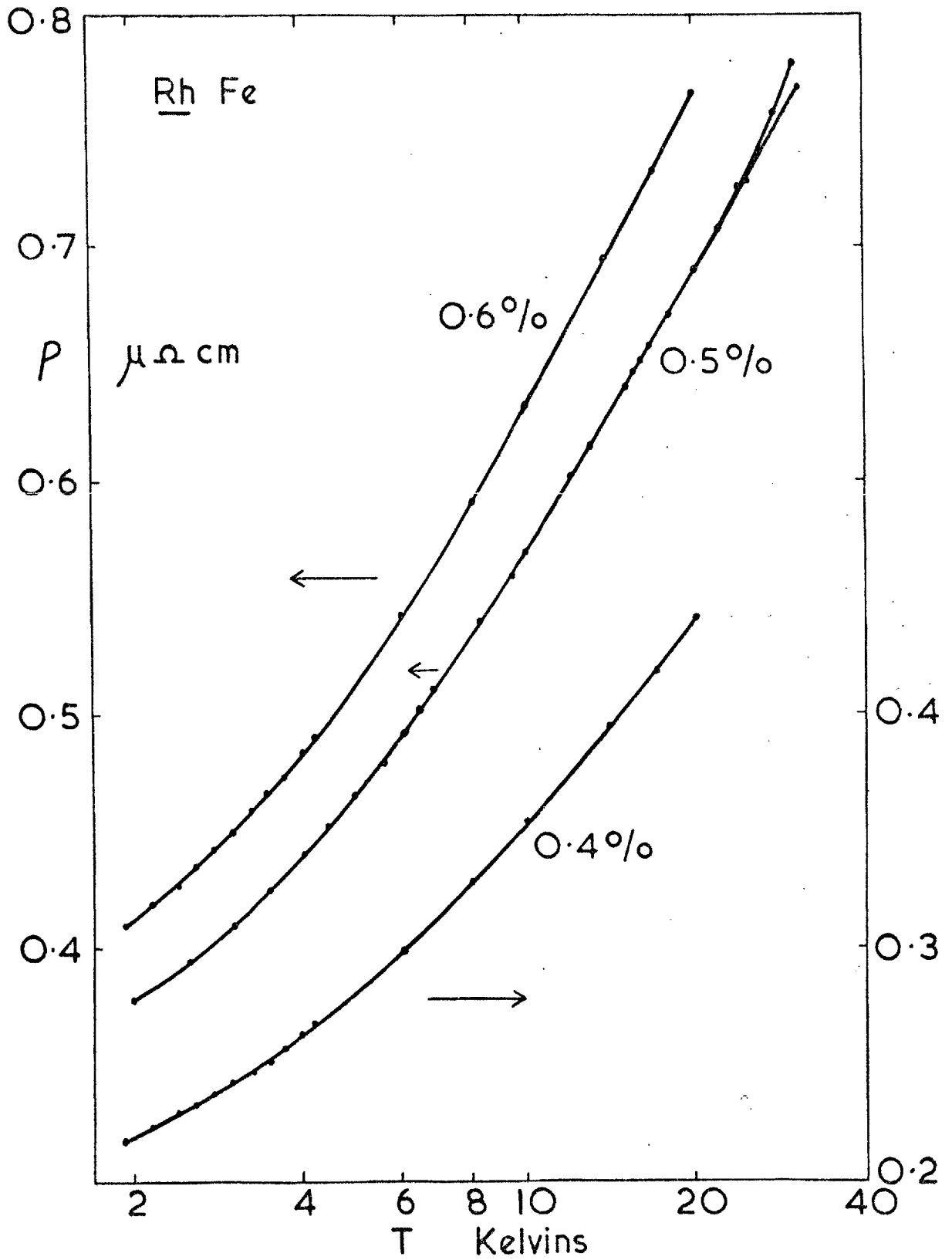


Fig 3.12. Resistivities of E II Rh - 0.5% Fe and E III Rh Fe containing 0.4 and 0.6% iron

the E II 0.5% sample and the E III 0.4% and 0.6% samples plotted against $\log T$. In no case does such a plot of the resistivity appear genuinely linear though the curvature above 7 K is much less pronounced. White and Woods' values for ρ_{Rh} are subtracted from the resistivity of the 0.5% sample above 20 K but the graph nevertheless deviates more strongly from a straight line.

In conclusion it would seem that the logarithmic dependence can neither be substantiated nor ruled out by the present data. The resistivity of pure rhodium is too significant in the dilute alloys and the effect could be masked by it or by deviations from Matthiessen's Rule, while in the more concentrated alloys the interaction effects could not only shift the universal curve to lower temperatures but also modify it so that no clear proportionality with either T or $\log T$ is observed. More conclusive results may possibly be obtained if an intermediate concentration, say with 0.2% Fe, were to be measured.

The last feature of the results for the rhodium based alloys which should be mentioned concerns the anomalous fall in resistivity below the T^2 law at low temperatures. It has been observed in Rh Co (fig 3.4) and in both samples of Rh Fe (figs 3.8 and 3.9) which were measured below 0.5 K. The effect may also be seen in other work; for example, the measurements of Laborde and Radhakrishna (unpublished) of a 0.2% Rh Fe sample plotted against T^2 show the depression below 0.2 K (their measurements of a 0.5% sample - 1971 - may not have extended to low enough temperatures). The data of Guertin et al. (1971) for Ir 0.5% Fe versus T^2 also show an effect below about 1.5 K and Oliveira and Foner (1971) found that in a Rh 1% Fe alloy the anomalous fall in resistivity occurred below 0.15 K, while the T^2 region, which would be suppressed to low temperatures, was not observed at all.

The temperature T_f at which the fall in resistivity occurs in Rh Fe does not seem to be sensibly related to the nominal concentrations

of the alloys. From the present data it might be supposed that the effect is genuinely due to scattering from isolated impurities since T_f and T_s are both higher in the 0.06% alloy ($T_f \sim 0.11$ K) than in the 0.5% alloy ($T_f \sim 0.05$ K). However T_f in the 0.2% Fe sample of Laborde and Radhakrishna is too high (0.2 K) to be consistent with this, and Oliveira and Foner's result for the 1% alloy ($T_f \sim 0.15$ K) cannot be explained on this basis both because T_f is too high, and because the T^2 dependence was absent. It seems more likely that the effect is caused by scattering from iron pairs which White and Swallow (1971) considered to account for the lack of a T^2 dependence in Oliveira and Foner's results. Near neighbour pairs of iron atoms are assumed to scatter as a single centre, but with a much reduced characteristic temperature since the lsf lifetime at such a centre is much longer. For alloys of less than 0.5% Fe the effect is small over most of the temperature range because the number of pairs is small and the temperature dependence of scattering by pairs is small compared with that of isolated atoms. The effect is only observed at very low temperatures where $d\rho/dT$ for the isolated solute atoms is small and the temperature dependence of the scattering from pairs of iron atoms is at its largest. The magnitude of the effect should be proportional to the square of the concentration and it is therefore significant that T_f is about four times larger in Oliveira and Foner's 1% alloy than in the E II 0.5% alloy. To account for the high T_f in the 0.06% and 0.2% alloys, however, it is necessary to postulate a higher than statistical probability for the occurrence of pairs or that the estimate of the concentration is in error. Since the 0.06% is in reality a failed 0.5% alloy, such an explanation is very plausible. Effects due to larger clusters of iron atoms may also be present, though they too are expected to be small and temperature independent over most of the range.

It may be noted here that similar effects were observed in dilute Cu Fe (Star 1972 a). He found deviations from the $(1-AT^2)$ dependence of the resistivity below 0.3 K even in samples containing 30 and 50 ppm of iron. These could be accounted for by a negative $\log T$ contribution to the resistivity just as if iron pairs were scattering with a very low Kondo temperature. It is remarkable that the effect should be observed at such low concentrations but the fact that it was larger in the 30 ppm than in the 50 ppm sample suggests that there was some inhomogeneity in the alloys.

CHAPTER 4

THE RHODIUM-IRON THERMOMETER

4.1 Introduction

One of the major achievements in the formulation of the International Practical Temperature Scale of 1968, the IPTS-68 (HMSO 1969, C R Barber 1969) was the inclusion of the range from the boiling point of oxygen (90.188 K) to the triple point of equilibrium hydrogen (13.81 K), using the platinum resistance thermometer as the interpolating instrument. At lower temperatures precise thermometry using a platinum thermometer becomes increasingly difficult because the temperature coefficient tends to zero and the resistance is too small to be measured sufficiently accurately at a current which does not cause excessive self-heating. There is therefore a need both for an interpolating instrument for a future IPTS below 14 K and for a resistance thermometer whose sensitivity and stability are high (~ 0.1 mK). As such a resistance thermometer must inevitably use an impure resistance element, however, it is unlikely to offer adequate batch-to-batch reproducibility to be the basis of a further extension of the IPTS.

Of the many substances which have been used as resistance thermometers at low temperatures (see reviews by Barber 1960, Rubin 1970), only two have achieved wide popularity, the carbon and doped germanium thermometers, in both of which the conductivity is dependent on the thermal excitation of charge carriers. The resistance of such thermometers therefore rises approximately exponentially as the temperature falls. The carbon thermometer probably provides the cheapest and simplest method of measuring temperature to 0.1%, while the germanium thermometer being more reproducible under thermal cycling, has found many applications in metrology. Even so, substantial changes in the calibrations of germanium thermometers have been found to occur after periods of apparent

stability. These may amount to 100-200 ppm in the resistance, equivalent to about 1 or 2 mK at 20 K and up to 0.5 mK at 4 K, and are probably due to small changes in bonding of the potential lead contacts. The second disadvantage of germanium thermometers is that at low temperatures the resistance rapidly becomes inconveniently high for measurement and the range of use is therefore restricted. A third disadvantage is that it is difficult to fit an accurate interpolation equation to the calibration data unless many points are obtained. It is proposed in this chapter that a rhodium-iron thermometer has certain advantages over a germanium thermometer in spite of its lower sensitivity. This is because of its wider range of use, its simpler characteristic and because it is not susceptible to sudden calibration shifts.

The suggestion that a rhodium-iron thermometer could prove useful at low temperatures was first made in the original paper (Coles 1964) describing the anomalous resistivity, and later by Oliveira and Foner (1971), and Rivier and Zlatic (1972 b). The latter authors also suggested that at very low temperatures (< 1 K) a platinum-iron thermometer may be more useful as the characteristic temperature T_{sf} is ~ 0.4 K compared with 12 K in Rh Fe, but the magnitude of the effect determined from the measurements of Loram et al. (1972) appears to be small compared with that in Rh Fe.

The first part of this chapter is concerned with the production of the rhodium-iron wire and a comparison of two designs of thermometer. The performance of the thermometer of the preferred design over the range 0.5 K to 20 K, which covers the range of accurate helium vapour pressure thermometry and overlaps with the lower end of the IPTS-68, is discussed. Possible uses of a rhodium-iron thermometer below 0.5 K and above 20 K are then considered, and conclusions are drawn concerning the likely role of the thermometer in the future.

4.2 The production of the rhodium-iron thermometer

(a) The wire

Naturally the first prerequisite for the rhodium-iron thermometer was the preparation of the alloy and the drawing of the wire. A wire of Rh - 0.5% Fe and 0.13 mm diameter was immediately available from Johnson Matthey Metals Ltd and was found to have resistivities of 7.25, 2.52 and $1.45 \mu\Omega\text{cm}$ at room temperature, 77.4 K and 4.2 K respectively, and thus a resistance ratio $R_{4.2}/R_{293}$ of 0.20. The resistivity at 4.2 K was very large compared with Coles' (1964) value of about $0.32 \mu\Omega\text{cm}$, though the mean temperature coefficient between 3.5 K and 4.2 K of $0.027 \mu\Omega\text{cm/K}$ was in approximate agreement with Coles' results. Thus it would appear that the resistivity due to the iron solute was superimposed on a large temperature independent resistivity of about $1.1 \mu\Omega\text{cm}$ due to the presence of extraneous impurities or crystal defects, with the result that the fractional sensitivity $(1/\rho)(d\rho/dT)$ was substantially reduced at low temperatures. Johnson Matthey's spectrographic analysis indicated that the total impurity content apart from iron was less than 400 ppm, most of which was iridium, and the wire had apparently been annealed at 900 °C for 15 minutes in an argon atmosphere. Such a specification should certainly produce excellent results, but these were not realised in practice.

Meanwhile Engelhard Industries Ltd had produced a trial sample of wire of diameter 0.13 mm and 20 cm in length, which gave resistivities of 6.32, 1.76, and $0.685 \mu\Omega\text{cm}$ at 293, 77.4 and 4.2 K respectively, a ratio $R_{4.2}/R_{293}$ of 0.11 and a fractional sensitivity $(1/\rho)(d\rho/dT)$ of about 5%/K at 4.2 K compared with Johnson Matthey's 2%/K. A subsequent batch of several metres of 0.13 mm diameter wire was better still, having a resistivity of $0.446 \mu\Omega\text{cm}$ at 4.2 K, a resistance ratio of 0.073 and a sensitivity of 6%/K at 4.2 K. This wire, labelled E II, was calibrated from 0.5 K to 90 K and the characteristic is plotted in fig 3.1.

After the successful testing of the Engelhard wire it was desirable to obtain finer diameter wire more suitable for resistance thermometers. Accordingly Engelhard drew the E II alloy down to 0.076 mm and 0.05 mm diameter, but these wires were found to have a large resistivity at 4.2 K ($\sim 1.8 \mu\Omega\text{cm}$) and a resistance ratio of 0.26. After annealing in vacuo for about 1 hour at 800 °C, however, $\rho_{4.2}$ was reduced to about 0.50 $\mu\Omega\text{cm}$ and the ratio to 0.09. Clearly the annealing treatment must be carefully judged as poor characteristics result if the anneal is inadequate (as was probably the case for the Johnson Matthey wire) while too much annealing produces excessive grain growth and weakens the wire (the 0.13 mm diameter E II wire suffered from this disability). Engelhard Industries studied the hardness and grain growth of the wire and found that after a 15 minute anneal at 1000 °C most of the hardness was removed, but that the grain size was only increased from about 10 microns to 15 microns, and this is now the recommended final annealing treatment. The complete process for the production of the wire is therefore roughly as follows:-

- (i) a calculated quantity of iron is chemically deposited on particles of pure rhodium of diameter less than 75 microns
- (ii) the powder is dried and pressed into bars 6 mm in diameter
- (iii) the bars are sintered in a hydrogen atmosphere at 1550 °C and remain at this temperature for several hours to allow the iron to dissolve fully
- (iv) the bars are hot swaged at 1500 °C to 1200 °C reducing the diameter to 3 mm in a hydrogen atmosphere
- (v) wires are hot drawn through tungsten carbide dies at 1200 °C to 500 °C to the finished size, again in a hydrogen atmosphere
- (vi) the wire is strand annealed in hydrogen for 15 minutes at 1000 °C.

Having prepared the wire the simplest test to determine its quality is to measure the resistivity at 293, 77.4 and 4.2 K. The resistance ratio $R_{4.2}/R_{293}$ should be in the range 0.08 to 0.10 - a higher value would indicate poor annealing while a lower value might suggest either that the annealing was overdone or that the iron had not fully dissolved. A combination of poor annealing and partial solution of the iron could give a reasonable value for the ratio but then the ratio R_{77}/R_{293} would be substantially lower than the expected value of ~ 0.25 . A better test, however, would be to measure the quantity of interest, namely the fractional sensitivity of the wire, which should be about $6\%/K$ at 4.2 K.

The choice of the iron concentration for the alloy used in the thermometers was based on Coles' results. The impurity resistivity was found to scale fairly well with concentration below 0.85% Fe so that if it is large compared with the residual resistivity of the pure rhodium, the fractional sensitivity is not strongly dependent on the concentration. The 0.5% alloy seemed to satisfy the requirements, and had also been the most thoroughly investigated. From the results of chapter 3 it may be deduced that an alloy of higher concentration would be less sensitive at higher temperatures, particularly in the 20-40 K range, because the characteristic temperature of the anomaly is depressed to lower values.

(b) encapsulation of the wire

The E II wire of 0.076 and 0.05 mm diameter which had been annealed at 800 °C was considered sufficiently good to be sent to H Tinsley and Co Ltd for the construction of rhodium-iron thermometers similar to the platinum capsule type of platinum resistance thermometers. The overall length, however, was restricted to 5 cm so that they could be accommodated in the ^3He cryostat; a photograph of such a rhodium-iron thermometer appears in Plate 3, page 5, together with a platinum thermometer and a germanium thermometer. Two variants of the design of the thermometer are sketched in fig 4.1. In type A, coils of rhodium-iron wire are

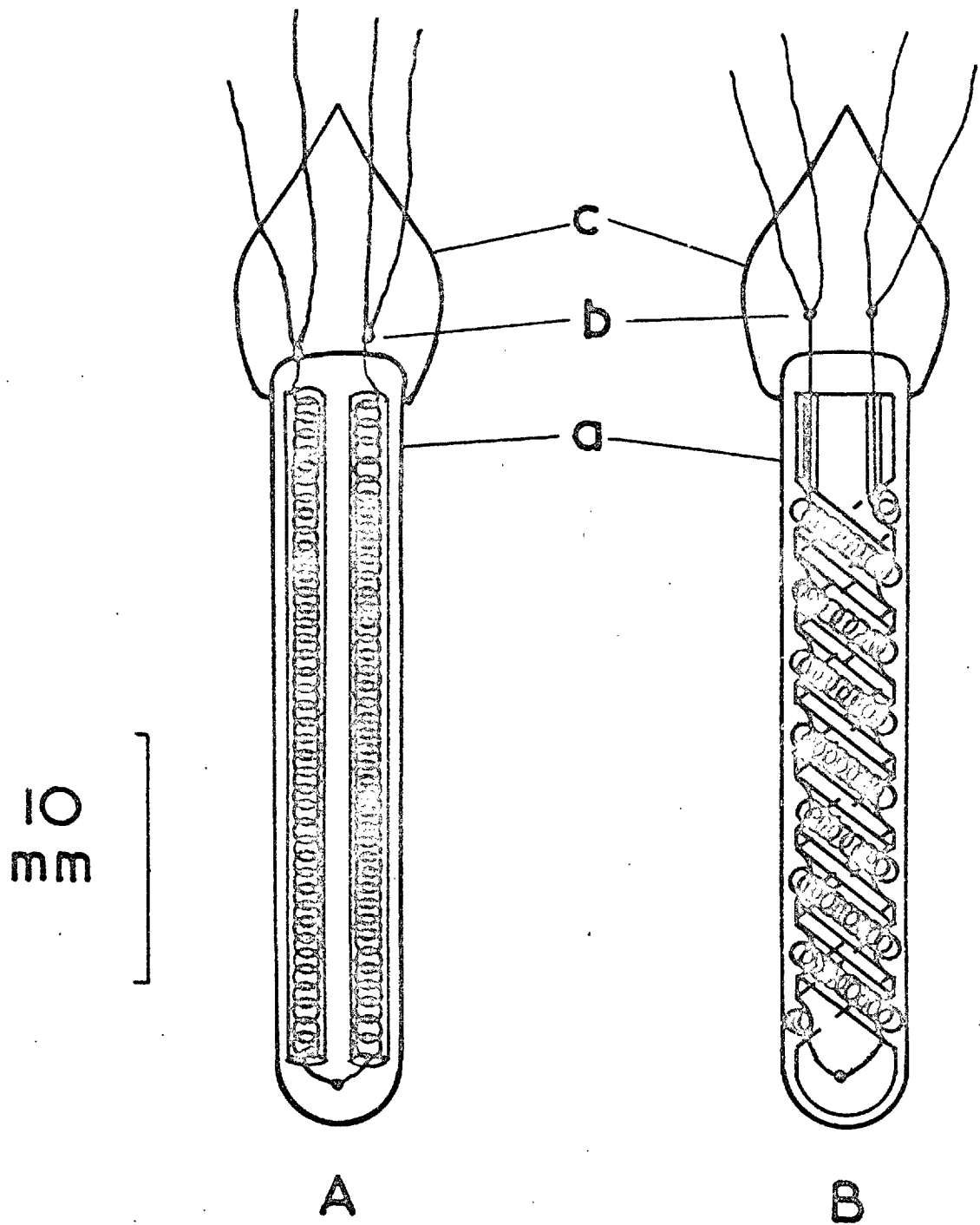


Fig 4.1. Two designs of rhodium-iron thermometer

are inserted into four glass tubes (two of which are shown) while in type B two coils are mounted on an alumina former. In both cases four platinum leads are flame welded to the rhodium-iron wire (b) and the assembly is inserted into a platinum sheath (a). The sheath and the leads are sealed in an atmosphere of helium by a glass bulb seal (c). The relative merits of the two designs have been discussed in a preliminary report (Rusby 1971) and the criterion used to judge which is superior was as follows. The self heating effect, ΔT , was measured for each thermometer during an immersion in liquid helium at 4.2 K and was plotted against the measuring current. The temperature resolution, δT , for a fixed voltage resolution of 10 nV, was plotted on the same graph and at a certain current there was a point of intersection where the heating effect was equal to the temperature resolution. The best design of thermometer was taken to be the one which gave the lowest value of δT at the intersection $\delta T = \Delta T$. As expected, the heating effect in the type B (alumina former) thermometer was lower than in the type A (glass tube) thermometer because the coils of wire are more enclosed in the latter design. However, with the glass tube construction it is possible to include about 50% more wire and thereby improve the temperature resolution at a given measuring current. The criterion outlined above was used to show that the advantage due to the extra resistance in the type A thermometer outweighed the disadvantage of poorer heat transfer, and the glass tube construction was therefore adopted for subsequent thermometers.

It is also advantageous to use the finest diameter wire available. If the diameter of the wire may be reduced by a factor α , the resistance is increased by a factor α^2 . The dissipation per unit surface area of the wire should not be increased, and as the surface area is reduced by α , the dissipation should be similarly reduced. Thus the voltage to be measured is increased, and the temperature resolution is improved,

by a factor $\sqrt{a}$. The 0.05 mm diameter wire was therefore preferred and thermometers of this wire and the glass tube construction gave the most satisfactory results. Typical values of their resistances were approximately

2.6 ohms at	0.5 K
3.5 ohms at	4.2 K
5.4 ohms at	20 K
6.7 ohms at	40 K
40 ohms at	273 K

A measuring current of 0.5 mA was found to give rise to a heating effect below 20 K of about 0.3 mK, which is acceptable for most purposes.

4.3 The performance of the rhodium-iron thermometer

(a) Sensitivity and stability

The resistivity of rhodium-iron and the fractional sensitivity $(1/\rho)(d\rho/dT)$ are plotted in figs 4.2 A and B as a function of temperature from 0.5 to 40 K and data for pure platinum are also included for comparison. The fractional sensitivity of rhodium-iron is seen to be at its highest in the helium range but to fall to a minimum of about 1%/K at about 28 K, above which temperature the 'ideal' resistivity of pure rhodium dominates the characteristic. In platinum the fractional sensitivity exhibits a high maximum of about 18%/K at 17 K below which the influence of the residual resistivity causes a substantial reduction in sensitivity.

The fractional sensitivity of the wire is translated into the voltage sensitivity of a thermometer on multiplying by the drop in potential across the thermometer at the appropriate measuring current. Typical voltage sensitivities are plotted in fig 4.2 C for rhodium-iron and platinum thermometers, and it may at once be seen that the low resistance of the platinum thermometer severely reduces its usefulness at low temperatures.

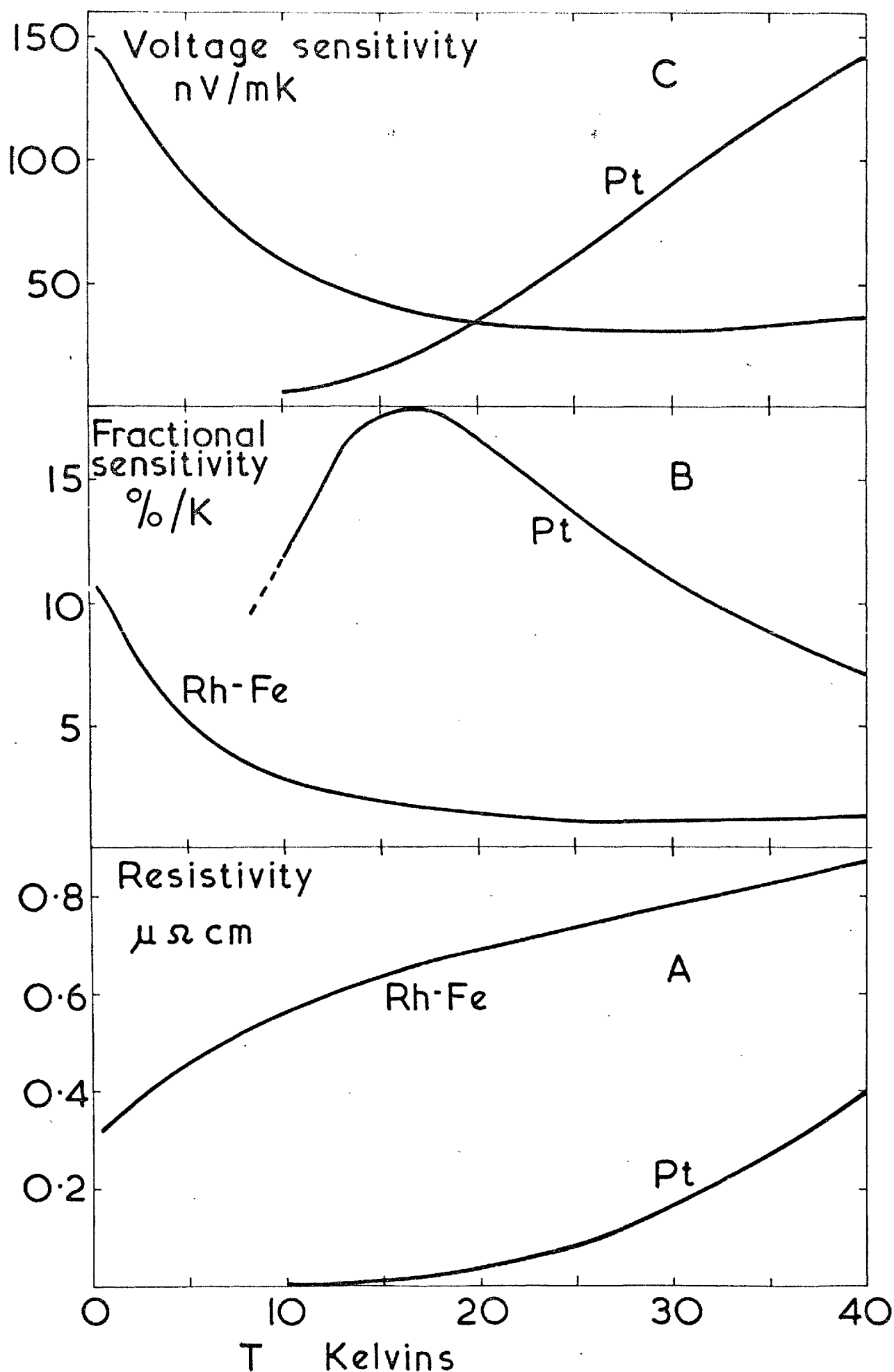


Fig 4.2. A The resistivities of rhodium - 0.5% iron and pure platinum
 B The fractional sensitivities $(1/\rho)(d\rho/dT)$ of Rh - 0.5% Fe and pure platinum
 C Typical voltage sensitivities of rhodium-iron and platinum resistance thermometers

The graph gives the voltage sensitivity in nanovolts/mK for a platinum thermometer of 25 ohms at 0 °C (and about 0.1 Ω at 20 K) at a measuring current of 2 mA. In practice the current is usually increased to 4 mA below 20 K to double the voltage sensitivity, but similarly as the resistance increases in the range 30-40 K the current must be reduced to 1 mA to avoid self-heating, and the voltage sensitivity is reduced by half. The rhodium-iron thermometer, of about 3.5 ohms at 4.2 K, was measured at 0.5 mA current over the whole range, and as expected the voltage sensitivity is least at about 28 K, but rises steadily as the temperature falls.

So far the rhodium-iron thermometer has been compared with the platinum thermometer because of their essential similarity. In practice its performance must be compared with that of the germanium thermometer as both are designed primarily for low temperature use. On the grounds of sensitivity the germanium thermometer is much superior. The fractional sensitivity of a thermometer of 1000 ohms at 4.2 K is about 40%/K at that temperature and about 10%/K at 20 K, while the voltage sensitivity at tolerable measuring currents may be greater than 100 nV/mK over this range (though in the high resistance circuit the resolution of small voltages is more difficult). However germanium thermometers are liable to undergo shifts in their calibrations of as much as 100-200 ppm in the resistance probably as a result of changes in the bonding of the potential leads to the chip. Since the sensitive element in the rhodium-iron thermometer is in wire form, small changes in the contacts are less important and a better stability may be expected. Using the triple point of water as a reference temperature, the drifts in the resistances of three of the first batch of thermometers were between 3 and 7 ppm over a period of 15 months and were all toward lower resistance values. At low temperatures three rhodium-iron thermometers, including one of the originals, were calibrated against the ^4He vapour pressure scale,

and after 11 months the drift in calibration was about -20 ppm in the resistance, equivalent to about 0.3 mK. Although a systematic effect in the measurements themselves cannot be ruled out it would seem that changes had occurred in the wire, possibly due to diffusion of iron towards grain boundaries or other iron atoms, or due to long term annealing. The effect at 20 K was not measured, but a similar change would be more serious (equivalent to about 1 mK). Clearly further tests after longer periods are required if a more accurate estimate of the drift rate is to be determined.

(b) Interpolation

An important feature of a resistance thermometer is its ability to give an accurate interpolation of values of temperature which lie between calibration points, and the relatively simple characteristic of the rhodium-iron thermometer suggests that it might be superior to a germanium thermometer in this respect. To test this, a rhodium-iron thermometer and three germanium thermometers were calibrated against the NPL gas thermometer between 2.5 K and 20 K, and against the ^3He and ^4He vapour pressure scales between 0.6 K and 4.2 K. The calibration data were fitted to polynomials which expressed the temperature T as a function of resistance R for the rhodium-iron thermometer, and $\log T$ as a function of $\log R$ for the germanium thermometers (for these the range did not extend below 1.6 K because of the high resistance values of greater than 10 k Ω which were encountered). The results for the rhodium-iron thermometer and the best germanium thermometer are presented in table 4.1. As the order N of the polynomial is increased, the standard deviation S of the fit from the data approaches the random error (~ 1 mK) much more quickly for the rhodium-iron than for the germanium thermometer data. Thus fewer points need to be taken in calibrating the former, and oscillations in the fit are less likely to occur. Less accurate interpolation is achieved, however, where the

	Rhodium-iron thermometer			Germanium thermometer		
	33 points, 0.6 K to 20 K			28 points, 1.6 K to 20 K		
N	S	δT	T	S	δT	T
3	18.6	33	6.5	79	154	7.6
4	1.4	4.2	18.2	23	43	1.6
5	1.4	4.0	18.2	22	44	18.2
6	0.88	1.6	0.6	6.0	14.7	2.0
7	0.72	1.4	2.6	3.4	5.9	7.6
8	0.72	1.3	3.4	0.95	1.5	2.0

Table 4.1

Comparison of fits to rhodium-iron and germanium
thermometer calibrations

N is the order of the polynomial

S (mK) is the standard deviation of the fit from the data

δT (mK) is the maximum residual

T (K) is the temperature of the maximum residual

range 25 to 30 K is included as this is complicated by the change in the sign of the second derivative.

(c) Magnetoresistance

In many applications it is desirable to make measurements of temperature in a magnetic field and therefore the magnetoresistance of a resistance thermometer is an important quantity. Comprehensive data are available for the effect in germanium and platinum (eg Neuringer et al. 1971) and show that it is large in both these materials at low temperatures. Typically a magnetic field of 30 kGauss produces in germanium an increase in resistance of about 40% at 4 K and in platinum a 100% increase at about 16 K, giving apparent temperature changes of about 1 K and 5 K respectively. By comparison the magnetoresistance of rhodium-0.5% iron is modest as measurements at 4.2 K and 2.1 K (fig 4.3) show, though the temperature equivalent nevertheless approaches 1 K at 30 kGauss.

As the magnetoresistance of rhodium-iron appears at first sight to be normal, it is interesting to compare these results with Kohler's rule:-

$$\frac{\rho_H - \rho_0}{\rho_0} = A \left(\frac{H}{\rho_0} \right)^2$$

where ρ_H and ρ_0 are the resistivities at field H and in zero field, and A is a constant. Although the results of fig 4.3 have this general character, when plotted against H^2 the data are observed to be curved. Contrary to the results of Coles (1964) and Murani and Coles (1972) no proportionality with H^2 was found even at low fields. Furthermore the effect at a given field but different temperatures did not scale with ρ_0^2 to better than 10%. The magnetoresistance of a sample of 'pure' rhodium wire, which contained about 40 ppm of iron, was found to be 36% at 4.2 K in a field of 30 kGauss and to be similarly curved

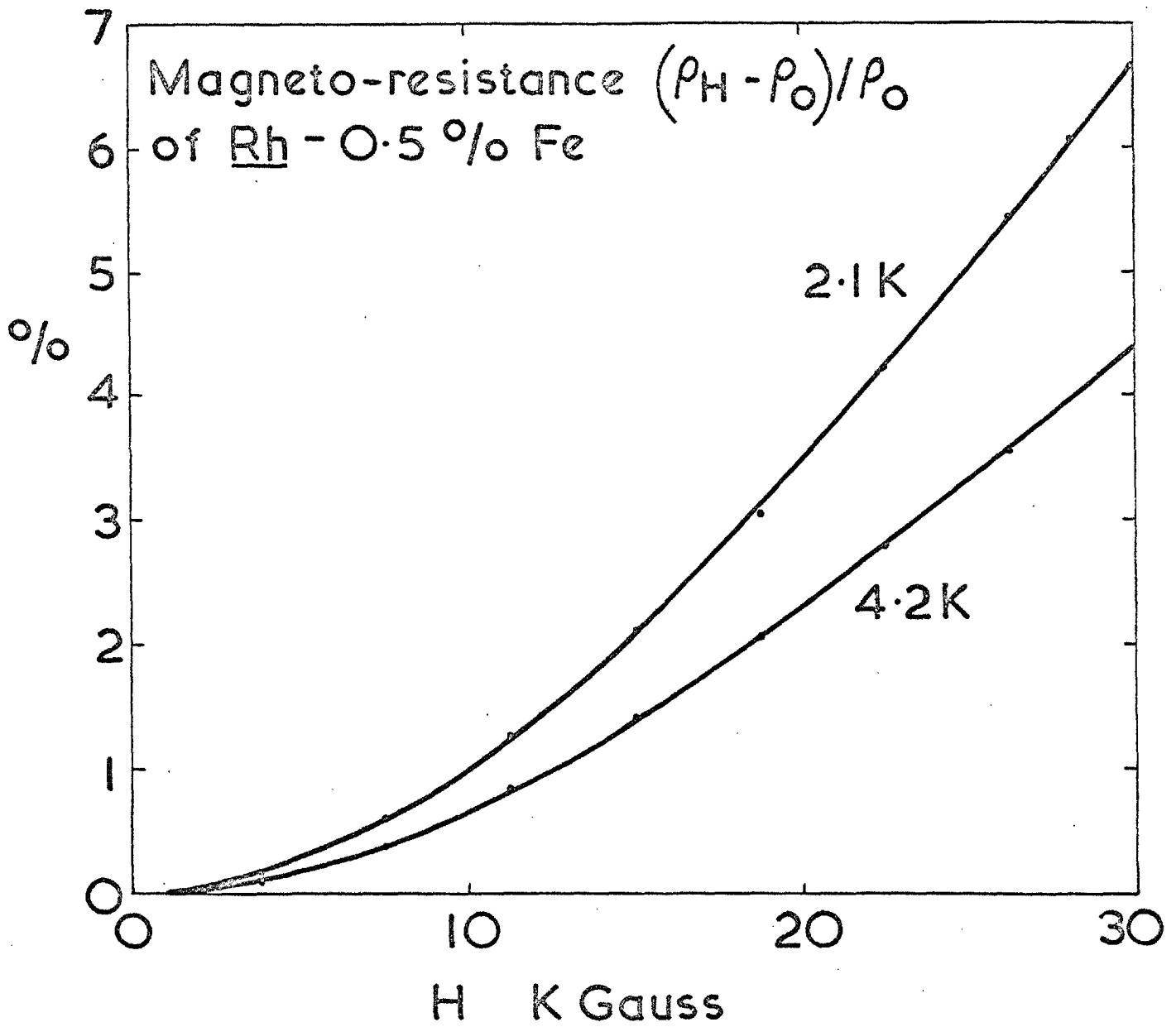


Fig 4.3. The magneto-resistance of rhodium 0.5% iron at 4.2 K and 2.1 K

when plotted against H^2 , though the results at a given field scaled with ρ_0^2 to better than 1%.

(d) Performance above 20 K.

Fig 3.1 shows that above about 30 K the resistivity characteristic of rhodium-iron is similar to that of pure rhodium and therefore the usefulness of the thermometer does not cease at higher temperatures. Indeed its sensitivity is not much less than that of a platinum thermometer and at 273 K both give resistance changes of about 0.4%/K. While it is not envisaged that the rhodium-iron thermometer will find applications in precision thermometry much above 20 K, it is evidently worth exploiting its wide range of use in less exacting measurements. The major difficulty in realising the full potential of the thermometer above 20 K is that a calibration would require many points unless a reference function could be employed, as for platinum in the IPTS-68, but the success of this procedure would depend on how well batches of the wire could be reproduced. From preliminary work using a reference function developed by Cryogenic Calibrations, it would seem that an accuracy of interpolation of 15-20 mK could be achieved from 2 to 273 K with only about 20 points, though a greater accuracy could be achieved at the lower end of the range.

For this kind of application it would be possible to sacrifice some of the resolution and the strain free mounting of the standards thermometer and reduce the size of the sensor considerably. It is possible to accommodate 1 metre of 0.05 mm diameter wire in a capsule of 3 mm in diameter and 20 mm in length. Such a rhodium-iron thermometer would have a resistance at 4.2 K of about 2 ohms, and operating at 1 mA with a voltage resolution of 0.1 μ V, the temperature resolution would be about 1 mK in the helium range, 3 mK between 20 and 40 K where the sensitivity is poorest, and 1 mK at 80 K and above, though the accuracy at higher temperatures may be limited in

practice by the need to measure the resistance to better than 10 ppm.

(e) Performance below 0.5 K

The sensitivity of the rhodium-iron thermometer (figs 4.2 B and C) is at its highest below 1 K, so what is the lower limit of its usefulness? Clearly the capsule type of thermometer described in section 4.2 would be susceptible to heating effects below 0.5 K as the ^4He exchange gas condenses and the vapour pressure becomes very small. In the experiment described in section 3.4 a length of 1 metre of 0.05 mm diameter Rh - 0.5% Fe wire was immersed in the dilute phase of the helium in the mixing chamber of the dilution refrigerator and its resistivity characteristic was measured down to 0.02 K. The reduction in the slope below 0.3 K is evident from fig 3.8 a, and the fractional sensitivity was determined to be $5\%/K$ at 20 mK. Furthermore the Kapitza boundary resistance is such that to avoid self heating of the wire at the lowest temperatures the dissipation in it must be very small. Thus as the temperature is lowered it is necessary to measure the resistance more and more accurately at lower and lower currents in order to achieve a given temperature resolution. In the experiment referred to, the resistance of the wire was about 2 ohms and the dissipation was 5×10^{-9} watts down to 40 mK so that with a voltage resolution of 10 nV the temperature resolution was about 2 mK. Below 40 mK the dissipation was reduced to 10^{-9} watts and the temperature resolution was then about 4 mK.

If, however, the length of wire is doubled and the diameter halved, then the resistance is increased by a factor of 8; these changes could probably be made, though no 0.025 mm diameter wire has yet been drawn. As the surface area is unchanged, the dissipation may also remain unchanged. Then the voltage to be measured is increased by a factor of $\sqrt{8}$ and a temperature resolution of 1 mK could be achieved down to

40 mK and possibly significantly lower. At 0.1 K, however, where a larger dissipation may be allowed, a measurement of temperature to 1 mK (1%) may be made with a voltage resolution of 0.1 μ V. It is evident that the usefulness of such a thermometer depends crucially on the voltage resolution of the measurements and on the length and diameter of the wire itself.

Although for a 0.5% Fe alloy it was found that at low temperatures a measurement of resistance to 50 ppm is required for a measurement of temperature to 1 mK (5% at 20 mK), it may be expected from the results of chapter 3 that a more concentrated alloy would be more sensitive at the lowest temperatures. The fractional sensitivity of the Rh - 1% Fe alloy of Oliveira and Foner (1971) was about 9%/K at 0.2 K and was still increasing with falling temperature. Furthermore the resistivity of the 1% alloy would be about twice as great as that of the 0.5% alloy (Oliveira and Foner did not give the absolute values of the resistivity). Thus for a given length and diameter of wire and at a given dissipation, the voltage to be measured would be increased by a factor of about $\sqrt{2}$, and the temperature resolution below 0.1 K would be improved nearly threefold. At even higher iron concentrations ($\sim 3\%$), however, the characteristic is again less sensitive (Murani and Coles 1970).

4.4 Conclusions

The rhodium-iron thermometer discussed in this chapter would seem to offer some advantages over alternative resistance thermometers in three areas:-

(i) in standards work below 20 K using the thermometer of the construction of fig 4.1 A, provided that periodic checks are made to test the stability of the resistance. The voltage sensitivity would be improved if a thermometer as large as a normal platinum thermometer (plate 3, page 5) could be accommodated.

(ii) In less demanding applications where a thermometer or a temperature control sensor is required to operate over a very wide range of temperature. Here a small version of the thermometer may prove useful.

(iii) In a dilution refrigerator, where a rhodium-iron thermometer could monitor the cooling from room temperature and be used accurately at least down to 0.1 K. In this application the wire is required to be in direct contact with the liquid helium, and possibly the most satisfactory thermometer would consist of the glass tubes of fig 4.1 A containing the strain-free coils of wire, but without the platinum sheath or glass seal. The thermometer would, of course, need to be calibrated, but its reproducibility from run to run should be excellent.

CHAPTER 5

VANADIUM AND VANADIUM-CHROMIUM BASED ALLOYS

5.1 Introduction

Considering the interest shown in the properties of iron when dissolved in binary Nb-Mo hosts (Matthias et al. 1960, Clogston et al. 1962, Sarachik et al. 1964) it is perhaps surprising that experiments were not made in the equivalent 3d system V-Cr-Fe. Nearly all the previous work on V Fe and V Cr alloys has been directed at determining the 3d band structure, ie the density of states $N(E_F)$, at an electron concentration of between 5 and 6 per atom. Thus Cheng et al. (1960) measured the specific heats of alloys of V Fe and V Cr, and Childs et al. (1960 and 1963) made susceptibility measurements in order to calculate $N(E_F)$ from the Pauli paramagnetic contribution. These experiments suggested that there is a minimum in the density of states between vanadium and chromium, as there is between Nb and Mo, and that iron and chromium dissolved separately in vanadium are nonmagnetic, the former up to about 20% and the latter over the whole range of compositions.

Although resistivity data for V Fe and V Cr alloys are not available from previous work, the superconducting transition temperatures, T_c , for a number of vanadium alloys have been measured, and some further data are given in table 5.1. The results from different sources do not always agree. In particular Muller (1959) found reductions in T_c in alloys of vanadium with 3d solutes which were too large to be ascribed to a reduction in the density of states, and suggested that interactions between localised spins and the conduction electrons were involved, ie that the alloys were magnetic. However the experiments of Matthias et al. (1960) on (Mo-Re)Fe alloys showed that the depression in T_c due to spin flip scattering is much larger

than is found in vanadium alloys, and more recent measurements of the transition temperatures including the present ones (see section 5.2) indicate that Muller's results were in error and that he had overestimated the effect.

The weight of evidence is therefore that 3d solutes are non-magnetic in vanadium, though whether this is due to the absence of localised d states on the solute atoms, or to the presence of non-magnetic virtual bound states is not clear. Resistivity measurements might detect spin fluctuation effects either in the d band or in a vbs and therefore such measurements were made on a number of dilute vanadium alloys below 77 K (section 5.2). As magnetoresistance data (Arajs and Dunmyre 1966) suggest that iron is magnetic in chromium, it is of interest to add chromium to vanadium to observe the appearance of the moment. Although resistance minima were found in molybdenum-rich (Nb-Mo) Fe alloys (Sarachik 1964) an anomaly of this type is not necessarily to be expected in the (V-Cr) Fe system. The excess charge on the iron atoms is between 2 and 3, depending on the host composition, and according to the phase shift arguments of Loram et al. (1972) this is just the region where the sign of the temperature coefficient of an anomaly is not easily predicted. In the event, no anomalies were detected in the resistivity of V-Cr alloys with $\frac{1}{2}\%$ Fe until the chromium content was 80%. The fact that resistance minima were observed in this and some other chromium-rich alloys (section 5.3) suggests that the analogy with the (Nb-Mo) Fe system is strong and that iron atoms give rise to virtual bound states in solution in V-Cr hosts which are split in the chromium-rich alloys where the density of states is low.

As the solubility of iron in vanadium-chromium alloys is good, it was possible to investigate the effect of increasing the concentration and in the ($V_{20}Cr_{80}$) host, 8% Fe was found to give rise to magnetic

ordering as evidenced by a resistance maximum at about 2 K. In the ($V_{10}Cr_{90}$) host, however, the reduction of the iron concentration from 0.5% to 0.1% was found to lead to an increase in the Kondo temperature so that the low temperature behaviour of the resistivity predicted by Rivier and Zlatic (1972 a) was observed. Chromium itself is antiferromagnetically ordered below about 311 K and the resistance anomaly associated with the Neel transition complicates any investigation of the resistivity of Cr Fe alloys (Arajs and Dunmyre 1966). However the addition of vanadium strongly depresses the Neel temperature and the resistivity measurements of Moller et al. (1965) suggest that at 5% V the transition lies well below 4.2 K. Therefore the resistivity of the ($V_{10}Cr_{90}$) host and its alloys should be free from complications of this origin.

5.2 Vanadium-rich alloys

The first objective of this series of experiments was to measure the resistivities of some alloys of vanadium with transition metal solutes to verify previous conclusions that such solutes are non-magnetic. A sample of pure vanadium and alloys of vanadium with 0.5% Fe, 0.5% Co, 2.0% Co, 0.8% Mo and a ternary alloy ($V_{90}Cr_{10}$)-Fe 0.5% were all prepared using the argon arc furnace. The suction-cast ingots of diameter about 2.3 mm were rolled or drawn to diameters of 0.5-1.0 mm and subsequently pickled in concentrated hydrochloric acid. The larger samples were carefully bent into an approximately circular shape, and after four platinum leads had been spot-welded to them the resistances of the samples were measured at room temperature and during an immersion in liquid nitrogen. The samples were then mounted in the cryostat and resistance measurements were made from the superconducting transition temperatures to an upper limit between 50 and 80 K, using a Diesselhorst potentiometer and a measuring

current of 5 mA. In most cases the samples were too irregular to allow a sufficiently accurate ($< 10\%$) estimate of the cross sectional area to length ratio to be made and the conversion to resistivity was therefore made using White and Wood's (1959) data for pure vanadium. It was assumed that $(\rho_{295} - \rho_{77.4})$ was the same in all the alloys as for pure vanadium, and having measured $(R_{295} - R_{77.4})$ for each, the values for A/l were calculated by division. This procedure should give a more accurate and a more consistent set of values for A/l than direct measurements, provided that the temperature dependence of the impurity contribution to the resistivity in the range 77 K to 295 K is small compared with the change of about $17 \mu \Omega \text{ cm}$ in the resistivity of pure vanadium. If the impurity resistivity is significantly temperature dependent above 77 K, it is probable that an effect will also be observed below 77 K in spite of an error in A/l ; if there is no such effect above 77 K, then the A/l value should be accurate.

Table 5.1 lists some data for the alloys and fig 5.1 shows that they all give approximately the same temperature dependence in the resistivity as pure vanadium; the resistivity of the $(V_{60} Cr_{40})$ Fe 0.4% sample is discussed below. Enlarged plots of the low temperature data failed to give any indication of an anomalous residual resistivity larger than the experimental accuracy of $\pm 0.005 \text{ m}\Omega$, and subtraction of the resistivity of pure vanadium yielded impurity resistivities from which no temperature dependence outside the limits of the probable error could be determined.

The resistivity of the $(V_{60} Cr_{40})$ Fe 0.4% alloy is also plotted in fig 5.1. This sample was suction-cast to a diameter of about 1.6 mm and was not rolled or drawn. Clearly its A/l value could not be deduced from the resistivity of pure vanadium but it was sufficiently regular in shape to allow a direct measurement of the ratio to $\pm 5\%$. A sample of $(V_{60} Cr_{40})$ was also suction-cast, but was highly irregular

Nominal composition	Actual composition	Dimensions dia x length preparation	$10^3 \times A/l$ $10^3 \times \text{cm}$	R_5 $\text{m}\Omega$	$(\rho_{77}-\rho_5)$ $\mu\Omega\text{cm}$	T_c K ΔT_c K
Pure V		0.9 mm x 151 mm rolled and drawn	0.45	8.3	2.39	4.86 0.1
<u>V</u> Fe (0.5%)	0.40% Fe	0.85 mm x 86 mm drawn	0.64	4.9	2.60	4.98 0.09
<u>V</u> Co (0.5%)	0.82% Co	0.44 mm x 38 mm rolled and drawn	0.38	16.1	2.51	4.50 0.05
<u>V</u> Co (2%)	1.66% Co	0.9 mm x 88 mm rolled	0.76	10.6	2.45	4.12 0.10
<u>V</u> Mo (0.8%)	0.8% Mo	0.9 mm x 131 mm rolled	0.51	6.3	2.43	4.99 0.04
(V ₉₀ Cr ₁₀) 0.5% Fe	(89.7/10.3) 0.62	.9 mm x 45 mm rolled	1.06	10.2	2.41	2.68 0.06
(V ₆₀ Cr ₄₀)	(61.8/38.2)	1.6 mm x 14 mm suction-cast ingot	10.9	1.6	1.49	~0.55 *
(V ₆₀ Cr ₄₀) 0.4% Fe	(61.6/38.4) 0.38	1.57 mm x 33 mm suction-cast ingot	5.8*	3.0	1.44	~0.55

Table 5.1 Compositions, dimensions and resistance data for vanadium-rich alloy samples

Note: T_c is the midpoint of the superconducting transition temperature and ΔT_c is the transition width.

* indicates A/l determined from the measured dimensions of the sample.

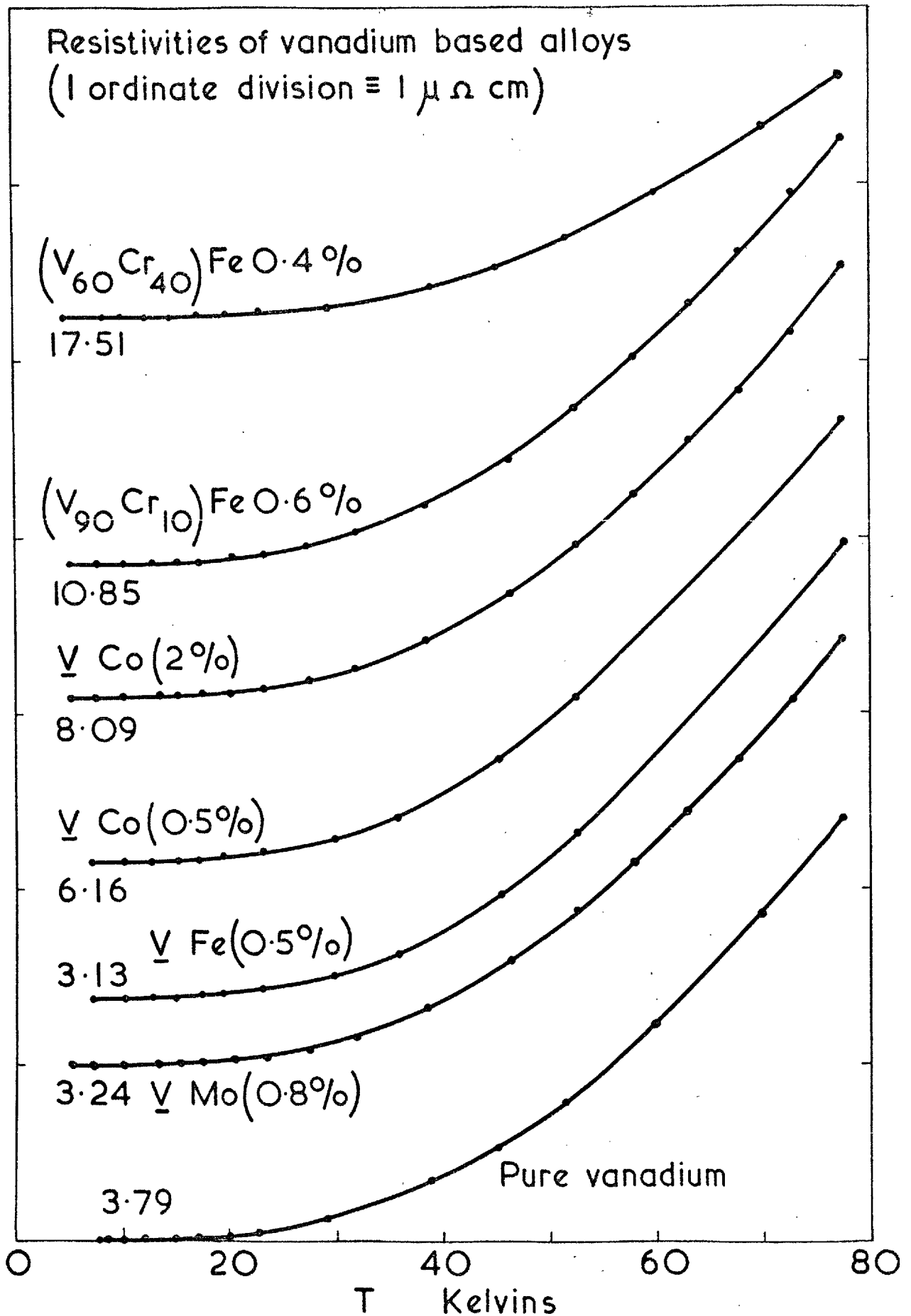


Fig 5.1 Resistivities of vanadium-rich alloys as a function of temperature, residual resistivities as marked

and its resistivity was therefore determined using the resistivity change ($\rho_{295} - \rho_{77}$) determined for the ($V_{60} Cr_{40}$) Fe 0.4% alloy. The values of ($\rho_{77} - \rho_5$) then obtained for these two alloys differed by only $0.05 \mu\Omega\text{cm}$, thus indicating the absence of a resistivity anomaly caused by the iron solute.

Transitions to superconductivity were observed in all the vanadium alloys mentioned so far, and since Matthias et al. (1960) found that local moments on iron atoms in (Mo-Re) Fe alloys produce strong depressions in T_c (of about 22 K/% Fe), the present alloys were investigated for this effect. The procedure was to monitor the ^3He or ^4He vapour pressure as the temperature drifted slowly through the transition. Readings were taken every half minute coincident with a potentiometer reading of the sample voltage which was made with the current alternately in the 'forward' and 'reverse' directions. Each transition, of up to 0.2 K width, was traversed in about $\frac{1}{2}$ to 1 hour and was then repeated in the opposite direction of temperature change. Three typical examples of transitions are plotted in fig 5.2, for the V Mo and the two V Co samples, showing that the points for different temperature directions are in good agreement except in V Mo (the worst case) where there is a shift of about 0.02 K between the points taken during rising and falling temperature. The transition temperatures and widths for all the samples are given in table 5.1. For those which lay above 4.2 K the Texas Instrument quartz spiral pressure gauge was used with the reference port at atmospheric pressure so that its absolute range was 1 to 2 atmospheres. Also, in order to prevent condensation of helium in the sensing tube, the helium level in the cryostat reservoir had to be below the vacuum flange. Therefore the silver block was filled with ^4He the day before the experiment and the reservoir level allowed to fall overnight. In the case of pure vanadium, the

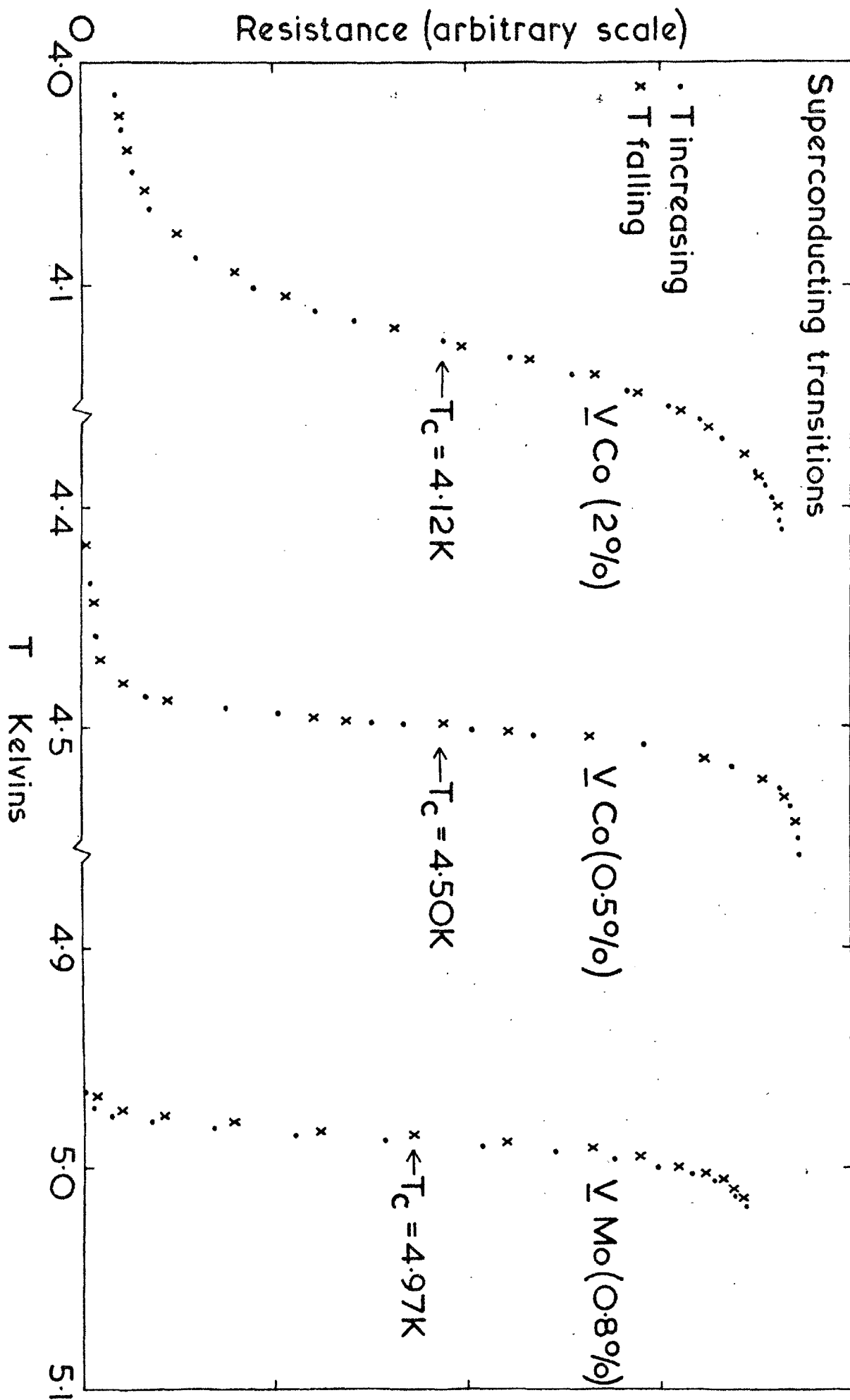


Fig 5.2 Transitions to superconductivity in three vanadium-rich alloys

transition was expected to be out of range of ^4He vapour pressure measurements, and was therefore monitored, less conveniently, using a rhodium-iron thermometer. On calculation of the results, however, the transition was found to be at about 4.86 K, depressed presumably by strains induced during cold working.

According to Muller (1959) the addition of about 8% chromium to vanadium depresses the transition temperature near to the absolute zero. This is in conflict with the results of Andres et al. (1969) and Hulm and Blaugher (1961) who found transitions in $(\text{V}_{90}\text{Cr}_{10})$ alloys at, respectively, 3.21 K and 1.9 K. The present $(\text{V}_{90}\text{Cr}_{10})$ -Fe 0.5% sample underwent a transition at about 2.68 K, which suggests that Andres' value for the composition without iron is the more reasonable. For his $(\text{V}_{60}\text{Cr}_{40})$ sample no transition was observed down to 0.37 K, but at the lowest temperature to which the $(\text{V}_{60}\text{Cr}_{40})$ -Fe 0.5% alloy could be taken in the ^3He cryostat (not below 0.6 K) there was a fall in the resistance to about $2/3$ of the normal residual value, which clearly indicated the onset of superconductivity. Later, four alloys - the $(\text{V}_{60}\text{Cr}_{40})$ and $(\text{V}_{40}\text{Cr}_{60})$ compositions, with and without 0.5% Fe - were attached to a copper post which communicated via a brush of fine copper wires with the liquid helium in the mixing chamber of the dilution refrigerator. During a cool-down both the samples of $(\text{V}_{60}\text{Cr}_{40})$ composition were found to undergo transitions in the region 0.45 K to 0.65 K (the experimental conditions were not favourable for a closer investigation of the transitions), but no indication of a transition was observed in the $(\text{V}_{40}\text{Cr}_{60})$ based alloys even when the helium temperature was 0.03 K.

These measurements show that iron impurity does not produce a large depression in the superconducting transition temperature in vanadium or in vanadium-chromium alloys of up to 40% Cr, and therefore the conclusion

drawn from resistivity measurements that iron is nonmagnetic in vanadium-rich vanadium-chromium alloys is substantiated.

5.3 Chromium-rich alloys

After the failure to observe a resistance anomaly due to iron dissolved in vanadium-rich V-Cr alloys, the proportion of chromium was progressively increased. Alloys of the 40-60, 30-70, 20-80 and 10-90 V-Cr compositions with and without approximately 0.5% Fe were suction-cast in the argon arc furnace to diameters of 1.55 or 1.9 mm, but as they were easily fractured no rolling or drawing was possible. The quality of the samples was variable; some were well formed cylinders while others were slivers, and only in a few cases were the samples unbroken over the whole length of the mould. As a result of the short lengths and large diameters, the resistances of the samples were small, typically 0.5 to 1 m Ω at low temperatures, and in order to be able to achieve a high resolution in the resistance measurements it was necessary to use a high measuring current and the 'stabaumatic' potentiometer with which voltage readings could be interpolated to 1 nanovolt.

It was not until the resistivity of the (V₂₀ Cr₈₀) Fe 0.5% sample was measured that an anomaly at low temperatures was observed. With the sample mounted in liquid helium in a 5 l storage vessel, a current of 200 mA could be used without self-heating and measurements of the sample resistance (about 1 m Ω) from 4.2 K to 2.2 K showed an increase of about 240 ppm with a scatter in the data of ± 10 ppm. In the same experiment the resistance of the (V₃₀ Cr₇₀) Fe 0.5% sample was found to be independent of temperature in this range to ± 10 ppm. Measurements made at currents of 30 mA in the ³He cryostat over a wide temperature range confirmed these results; a resistance minimum was observed in the (V₂₀ Cr₈₀) Fe 0.5% sample at about 14 K, but none was

detected in either the $(V_{30}Cr_{70})$ or $(V_{40}Cr_{60})$ compositions with 0.5% Fe. A very pronounced minimum was subsequently detected in the resistance of the $(V_{10}Cr_{90})$ Fe 0.5% alloy.

The effect of interactions between solute atoms was investigated by increasing the iron concentration to 2%. In the $(V_{20}Cr_{80})$ host the minimum was much deepened and a pronounced resistance minimum was also observed in the $(V_{30}Cr_{70})$ host. The $(V_{40}Cr_{60})$ Fe 2% alloy, however, showed a normal temperature independent residual resistivity. Interaction effects were further examined by increasing the solute concentration in the $(V_{20}Cr_{80})$ composition to 5% and 8% Fe, in which alloys the resistivity behaviour associated with spin glass ordering (as for example in Cu Mn) was observed. In the $(V_{10}Cr_{90})$ host the iron concentration was reduced to about 0.1% in order to observe the resistivity behaviour of a truly dilute alloy, and it was found that the spin fluctuation temperature was sufficiently high to allow a $(1 - AT^2)$ dependence to be detected.

Table 5.2 lists some of the relevant data for each sample. A major problem with such irregularly shaped samples was the conversion from resistance to resistivity. Of all the samples only four (including the $(V_{60}Cr_{40})$ Fe 0.5% sample) were sufficiently regular to allow a measurement of the mean cross sectional area to be made with an accuracy of better than 10%, and for the remainder an estimate of A/l was made using values of $(\rho_{295} - \rho_{77})$ obtained for these four samples and assuming that at any given V-Cr composition this quantity does not vary with the iron content. Fig 5.3 gives the values of $(\rho_{295} - \rho_{77})$ either measured or assumed for the range of V-Cr alloys, from which conversion factors were deduced by dividing by the appropriate resistance change $(R_{295} - R_{77})$. The shortcomings of this procedure are illustrated by comparing the consistency of the conversion factors for two alloys of the $(V_{10}Cr_{90})$ composition. A 10%

Nominal composition	Actual composition	Dimensions dia x length	$10^3 \frac{A}{l}$ $10^3 \times \text{cms}$	$R_{L.2}$ m Ω	$(\rho_{77} - \rho_{L.2})$ $\mu \Omega \text{ cms}$
(V ₄₀ Cr ₆₀)	(38.6/61.4)	1.55 mm x 16 mm	11.6	1.16	1.21
(V ₄₀ Cr ₆₀) 0.5% Fe	(38.7/61.3) 0.45	1.55 mm x 18 mm	11.6	1.21	1.08
(V ₄₀ Cr ₆₀) 2% Fe	(40.2/59.8) 1.72	1.9 mm x 27 mm	13.9	1.05	1.03
(V ₃₀ Cr ₇₀)	(29.8/70.2)	1.55 mm x 14 mm	12.9	0.88	0.95
(V ₃₀ Cr ₇₀) 0.5% Fe	(29.9/70.1) 0.50	1.55 mm x 14 mm	22.5	0.55	0.92
(V ₃₀ Cr ₇₀) 2% Fe	(29.6/70.4) 1.84	1.9 mm x 32 mm	10.2	1.48	0.87
(V ₂₀ Cr ₈₀)	(19.7/80.3)	1.9 mm x 24 mm	14.1	0.55	0.85
(V ₂₀ Cr ₈₀) 0.5% Fe	(20.6/79.4) 0.41	1.9 mm x 28 mm	9.35	1.04	0.80
(V ₂₀ Cr ₈₀) 2% Fe	(19.9/80.1) 1.86	1.9 mm x 28 mm	3.61	4.70	0.60
(V ₂₀ Cr ₈₀) 5% Fe	(20.2/79.8) 4.74	1.9 mm x 21 mm	3.85	6.27	0.17
(V ₂₀ Cr ₈₀) 8% Fe	(20.2/79.8) 7.80	1.9 mm x 36 mm	6.64	4.89	0.35 ₃
(V ₂₀ Cr ₈₀) 8% Fe	(20.4/79.6) 7.77	1.9 mm x 45 mm	10.53*	4.46	0.36 ₄
(V ₁₀ Cr ₉₀)	(9.8/90.2)	1.9 mm x 26 mm	9.10	0.54	0.68
(V ₁₀ Cr ₉₀) 0.1% Fe	(9.8/90.2) 0.13	1.9 mm x 35 mm	8.97* 7.91	0.75	0.60
(V ₁₀ Cr ₉₀) 0.5% Fe	(10.0/90.0) 0.45	1.9 mm x 37 mm	8.06*	0.98	0.55

Table 5.2 Composition, dimensions and resistance data
for chromium-rich alloy samples.

Note: * indicates A/l determined from measured sample dimensions.

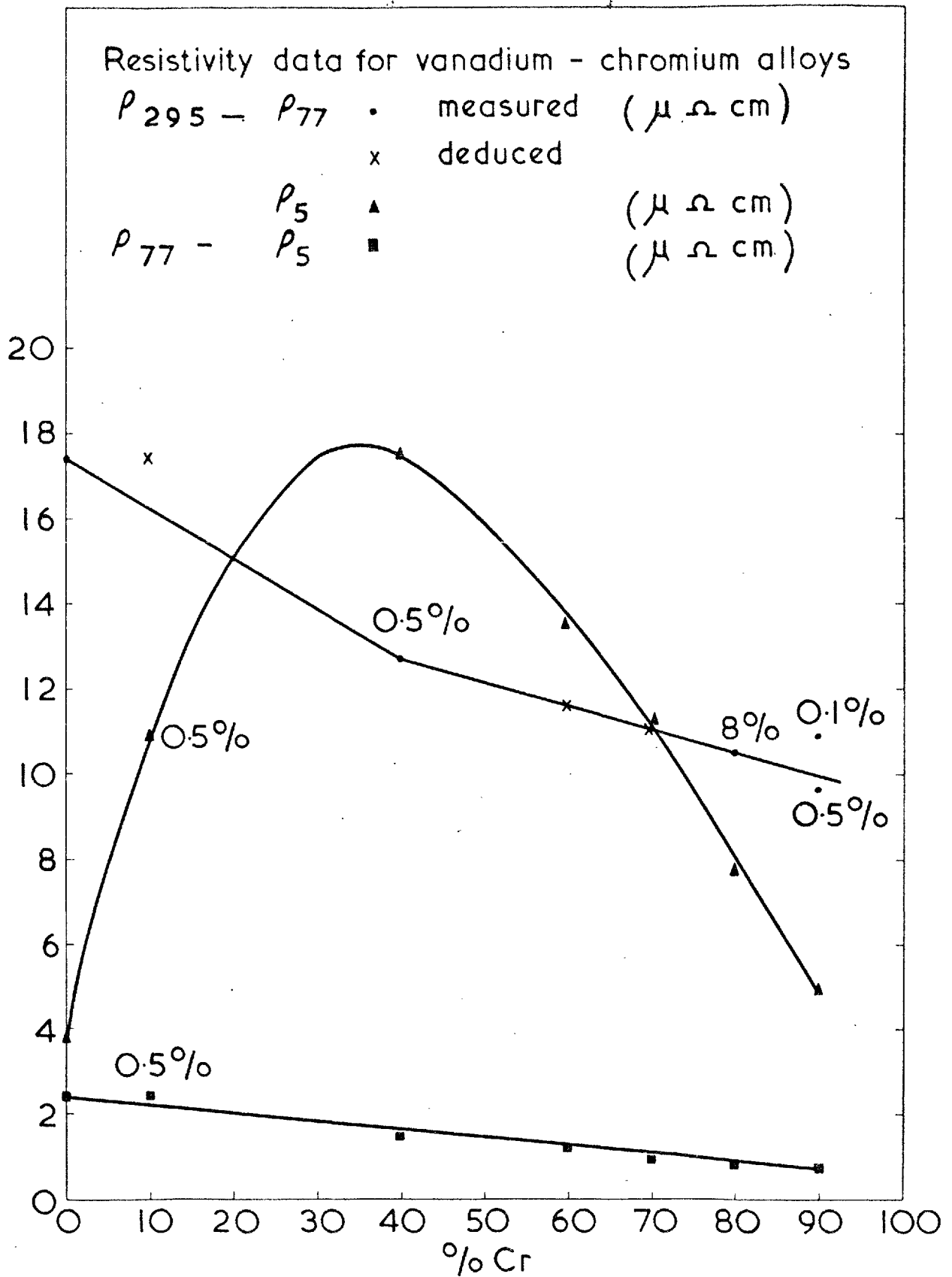


Fig 5.3 Resistivity data for V-Cr alloys. Points marked with a percentage indicate data for alloys containing that proportion of iron

measurement of A/l was possible for both the 0.5% and 0.1% samples, but the measured value for the 0.1% sample differed by 12% from the value deduced using the measured resistivity change ($\rho_{295} - \rho_{77}$) of the 0.5% sample. Such errors are to be expected, though in using the same value of ($\rho_{295} - \rho_{77}$) for all alloys of a given host composition it is possible that errors in the conversion factors for those alloys would all be of a similar magnitude. Fig 5.3 also shows values of the resistivities at 5 K, ρ_5 , and ($\rho_{77} - \rho_5$) for the different V-Cr compositions (points marked with a percentage indicate that the value was determined for an alloy containing that amount of iron).

Having made conversions to resistivity, albeit not very accurately, it was possible to estimate the magnitude of the impurity resistivity due to iron in V-Cr alloys more quantitatively. Fig 5.4 shows the resistivities of alloys of different host compositions containing approximately 0.5% Fe from which it may be seen that the anomaly is about five times greater in the ($V_{10}Cr_{90}$) composition than in ($V_{20}Cr_{80}$). The resistivities of alloys of 0, 0.5 and 2% iron in the ($V_{40}Cr_{60}$) host were plotted against temperature, but on subtraction of the host resistivity from the resistivities of the two alloys containing iron, it appeared that the impurity contribution fell rapidly with increasing temperature. However it is believed that the measurements of the host resistivity were erroneous (though the source of the error is obscure: the measurements were reproducible after the experiment at 295 and 4.2 K) and that no real impurity effects were observed even in the 2% Fe sample. The basis for this conclusion is that the magnitude of the apparent effect was the same in both samples; that is, the difference between the resistivities of the 0.5 and 2% Fe samples was approximately constant (to within the experimental accuracy) over the whole temperature range, and this would not be the case if the impurity resistivity were a function of temperature.

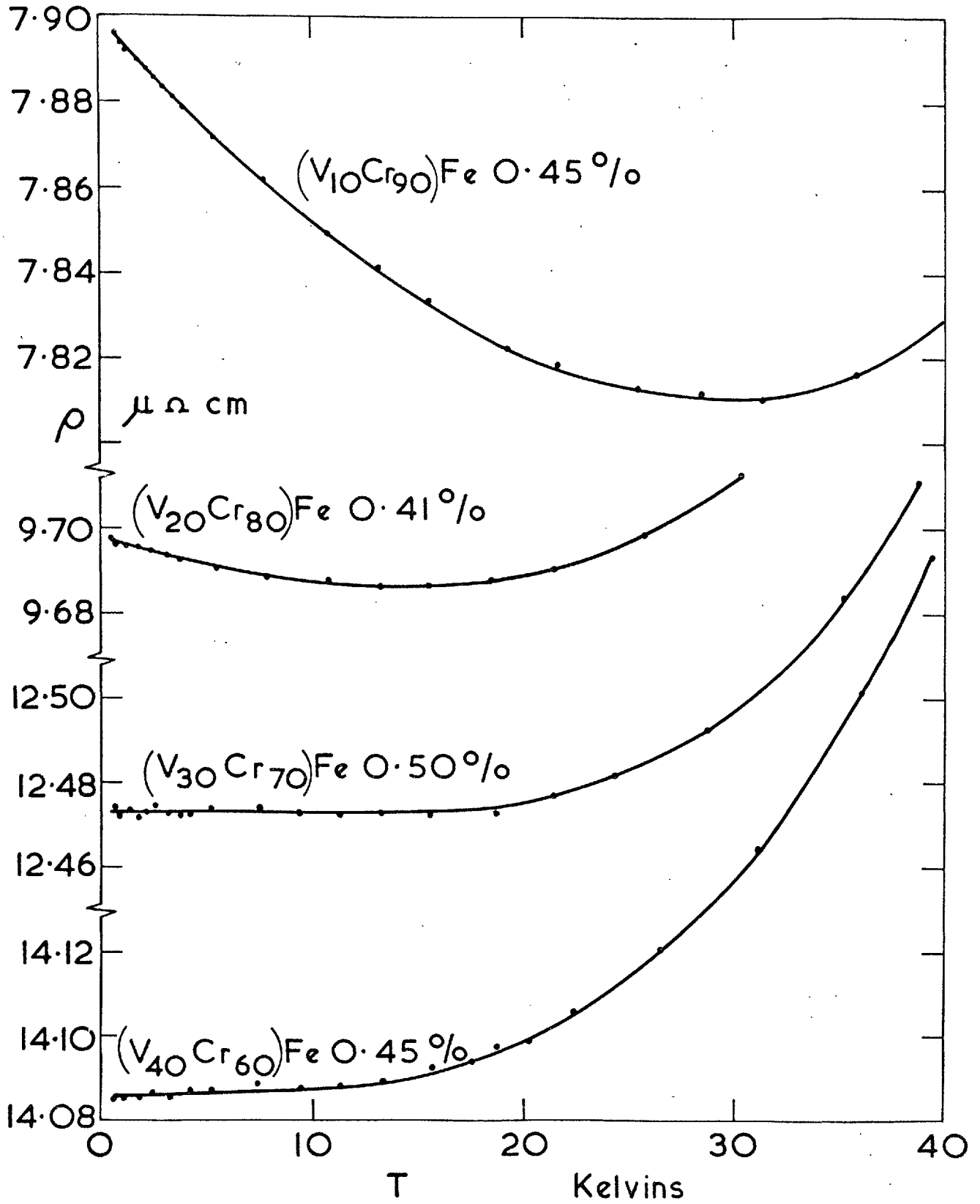


Fig 5.4 Resistivities of vanadium-chromium alloys containing about 0.5% iron

In fig 5.5 the results for the resistivities up to ~ 40 K of the alloys of the ($V_{30}Cr_{70}$) host composition with 0, 0.5 and 2% Fe are presented. As noted above, the resistivity of the 0.5% Fe alloy showed no temperature dependence in the helium range, but at higher temperatures the resistivity increase ($\rho_T - \rho_5$) was somewhat smaller in this alloy than in the host, which therefore suggests an impurity resistivity that decreases as the temperature increases. The magnitude $\delta\rho$ of the decrease ($\sim 0.015 \mu\Omega\text{cm}$ at 40 K and $\sim 0.03 \mu\Omega\text{cm}$ at 77 K) lies within the possible error in the calculation of the absolute resistivities, but if $\delta\rho$ arises solely from this cause it should be a constant proportion of ($\rho_T - \rho_5$). This is not observed, ($\rho_T - \rho_5$) being ~ 0.08 and $\sim 0.92 \mu\Omega\text{cm}$ at 40 K and 77 K respectively. It is therefore possible that $\delta\rho$ is due in part at least to a genuine impurity effect of very high Kondo temperature, but if so it is very small compared with that which causes the deep minimum observed in the resistivity of the 2% Fe sample. It would seem that interactions between iron atoms lead to a stabilisation of the magnetic moments and a large reduction in the Kondo temperature. There is no indication of a $(1 - AT^2)$ resistivity down to 0.5 K, but at high temperatures the subtraction of the phonon contribution to the resistivity shows that the impurity resistivity has the appearance of a $\log T$ dependence up to about 25 K, beyond which it falls more rapidly, probably because of errors in the absolute resistivities.

The stabilisation of the local moments on the solute iron atoms was more extensively investigated in the ($V_{20}Cr_{80}$) host. Measurements of the resistivities of the host (ρ_{host}) and four alloys containing from 0.4% up to 8% Fe are plotted in figs 5.6 and 5.7. In each case the effect of the iron impurity is to produce a minimum in the resistivity which after subtraction of the phonon contribution

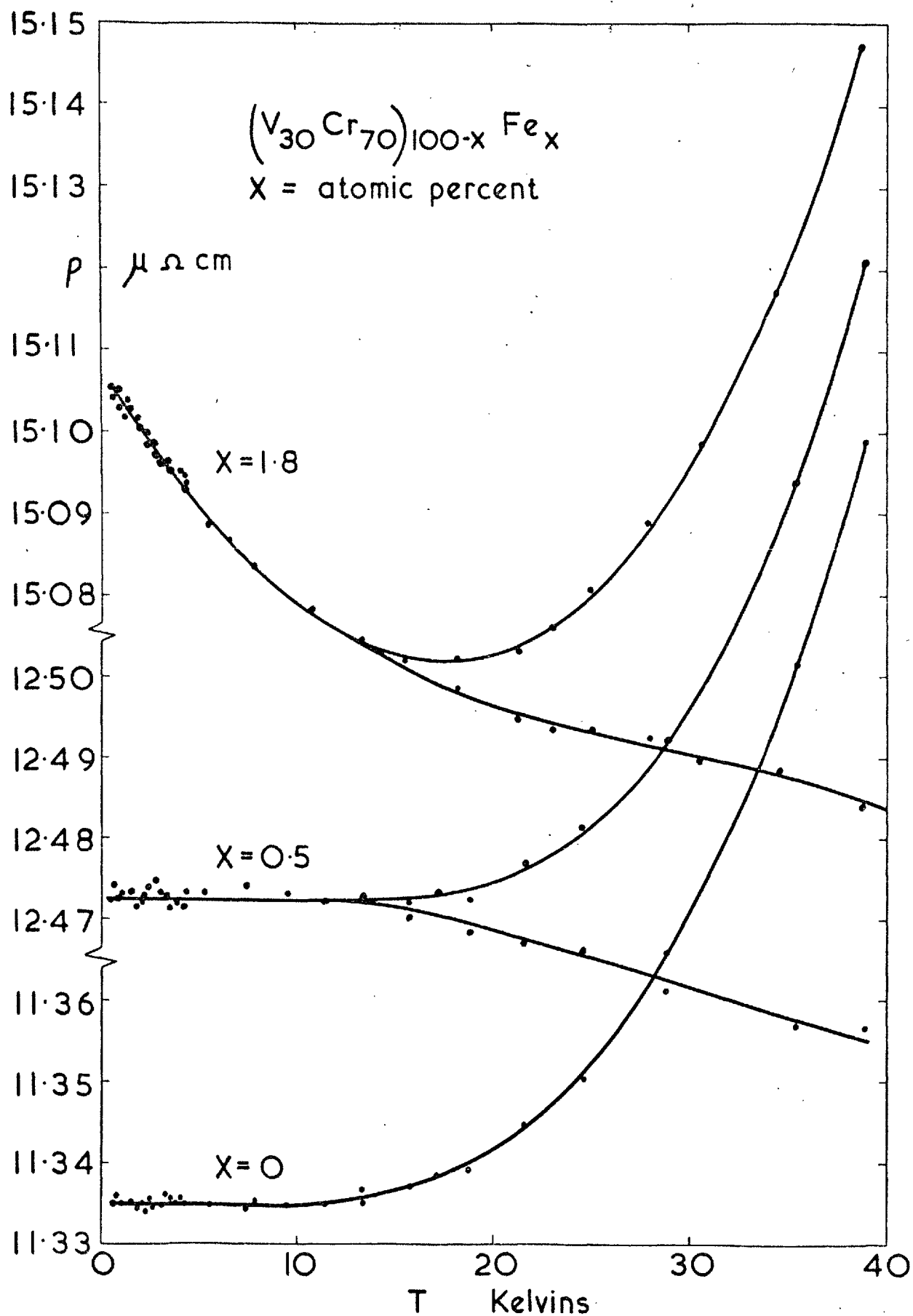


Fig 5.5 Resistivities of alloys of $(V_{30}Cr_{70})$ containing 0, 0.5 and 1.8% iron

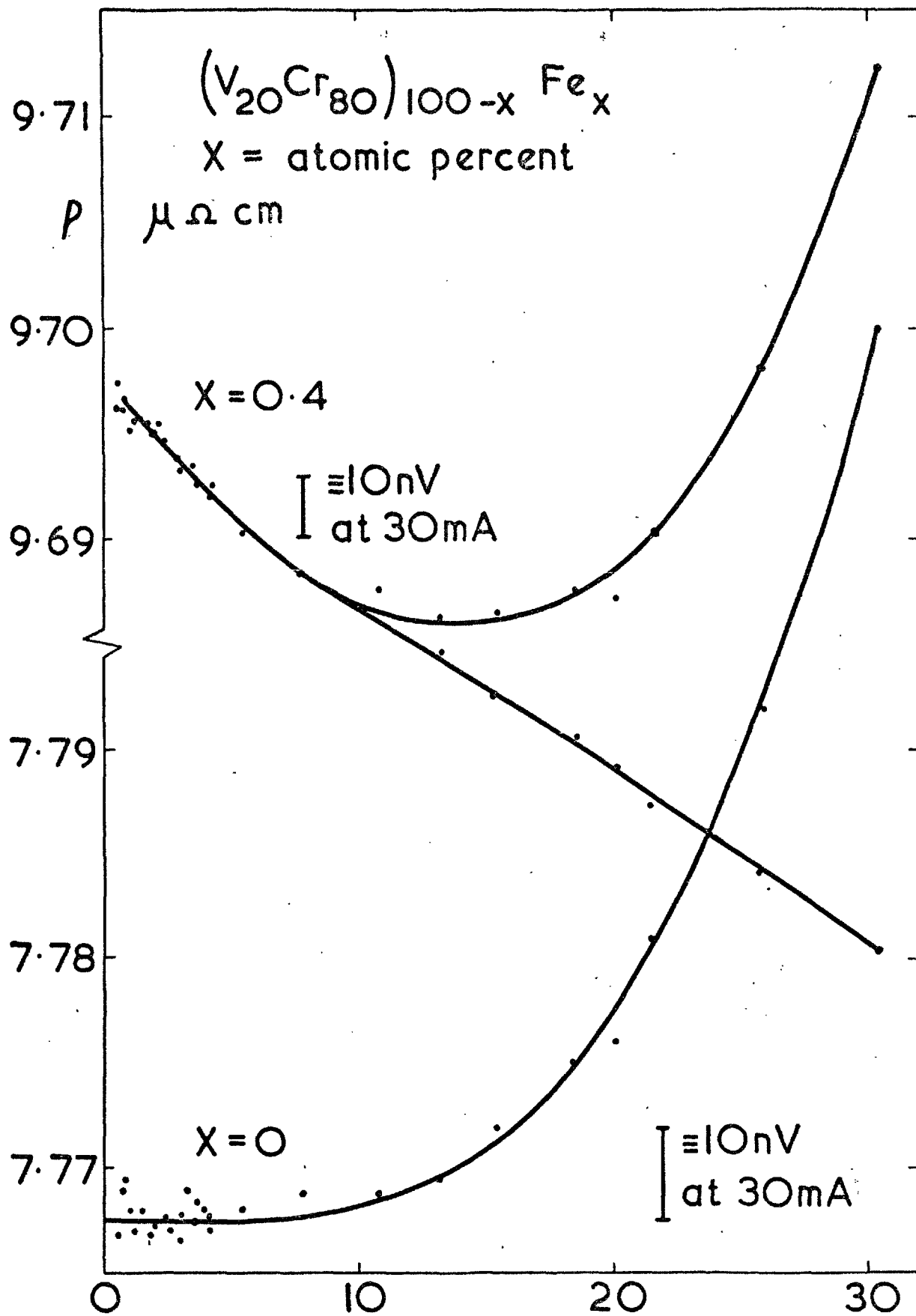


Fig 5.6 Resistivities of $(V_{20}Cr_{80})$ and $(V_{20}Cr_{80})Fe\ 0.4\%$

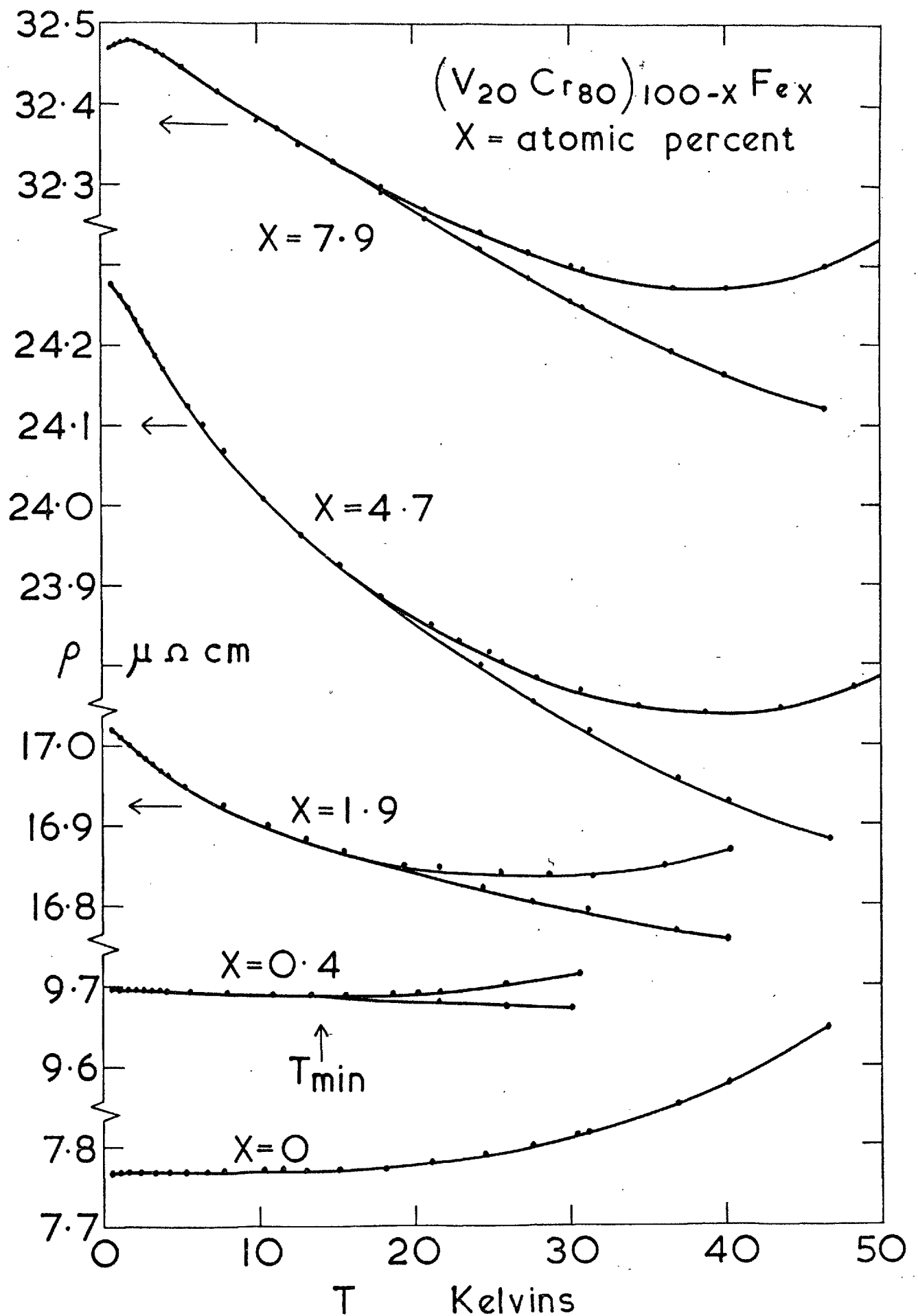


Fig 5.7 Resistivities of alloys of $(V_{20}Cr_{80})$ containing up to 7.9% iron

leaves a term with the approximate character of a negative log T dependence. The depth and the temperature of the minima were found to increase with iron concentration up to 5%. At 8% however the interactions between iron atoms are sufficiently strong to produce short range magnetic ordering and a resistance maximum at about 2.0 K. Ordering effects were also observed in the resistivity of the 5% alloy which gave a definite indication below 1 K of approaching a maximum at lower temperatures. A useful quantity for measuring the effect of interactions is the impurity resistivity per percent of iron $\Delta\rho/C$, where $\Delta\rho = \rho - \rho_{\text{host}}$. In fig 5.8 the resistivities at 4.2 K of the ($V_{20}Cr_{80}$) based alloys and the values of $\Delta\rho/C$ calculated from them are plotted as a function of iron concentration. Although the peak in $\Delta\rho/C$ is reached at 1.9% Fe, as is reasonable, the values are subject to large errors resulting from the uncertainties in ρ and ρ_{host} . An alternative estimate of the magnitude of the impurity effect, less well founded in principle though probably more realistic in practice, may be made from the maximum negative slope of the resistivity per percent of iron, $-(1/C)(d\rho/dT)_{\text{max}}$. This quantity is also plotted in fig 5.8, multiplied by 1000, and since it may be determined independently for each sample it is more accurately calculable than $\Delta\rho/C$. The stabilisation of the moment between 0.4% and 1.9% Fe is now more evident and the tendency toward magnetic order between 1.9% and 5% is seen to be gradual, becoming pronounced only above 5% Fe.

Although the temperature dependence of the impurity resistivity due to iron in the ($V_{20}Cr_{80}$) composition is larger than in previously investigated hosts, the nature of the temperature dependence in the dilute limit was not clearly established. At the higher temperatures the resistivities all have the appearance of a logarithmic variation with temperature, but the scatter in the data for the 0.4% Fe sample,

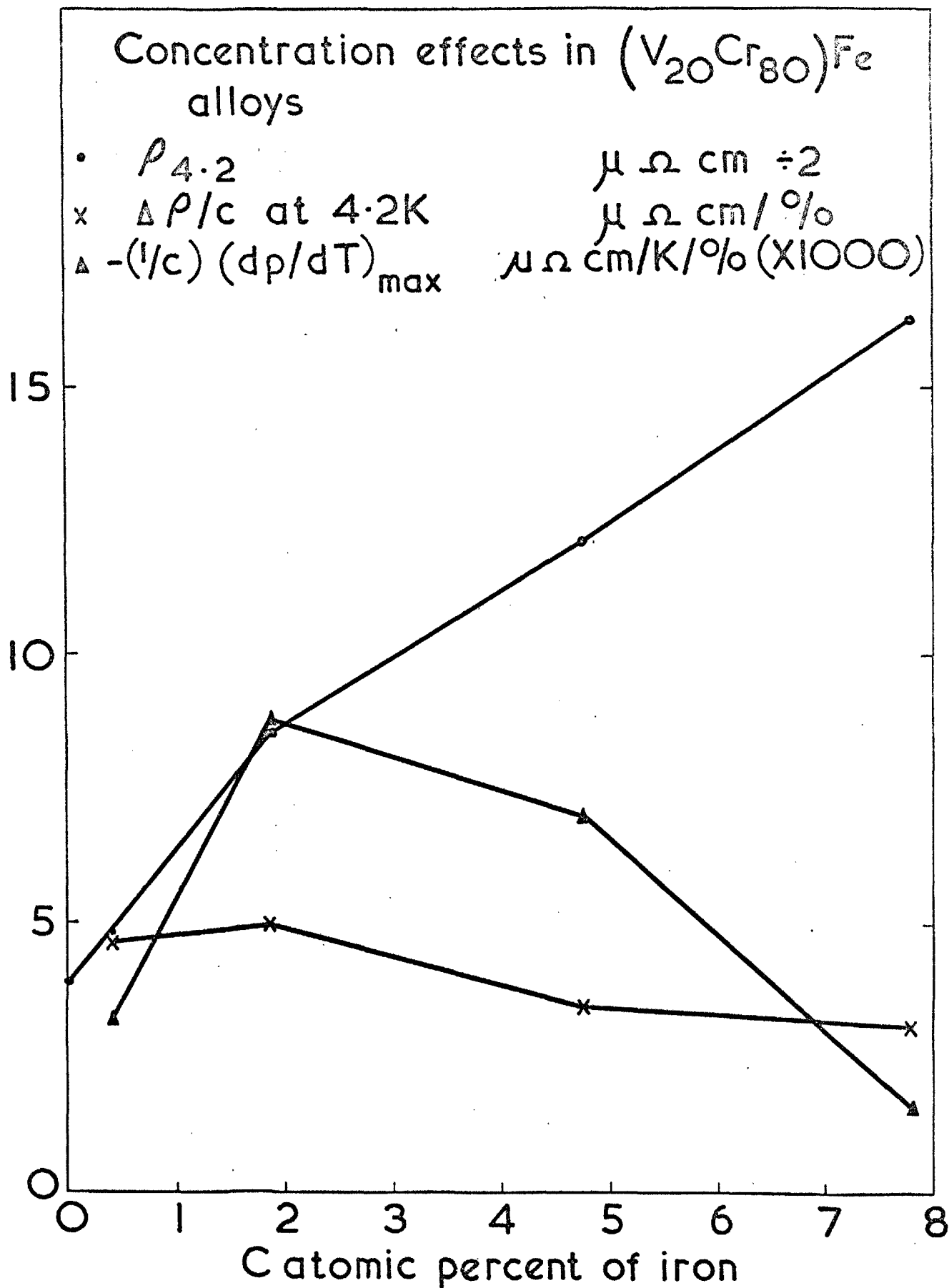


Fig 5.8 Analysis of resistivity data for $(V_{20}Cr_{80})Fe$ alloys as a function of iron content

for which the Kondo temperature is expected to be highest, was sufficiently large to obscure a linear region or a $(1 - AT^2)$ dependence which might be present at low temperatures. However fig 5.9 shows that a linear region of slope $- 0.016 \mu\Omega\text{cm/K}$ was observed in the resistivity of the 1.9% Fe sample in the helium range. It is also possible that the $(1 - AT^2)$ region was encountered in this sample below 1 K, but in view of the probable experimental error such a deduction is not justified.

The temperature dependence of the impurity resistivity per iron atom is further increased in the $(V_{10}Cr_{90})$ host, and the data for the three samples containing 0, 0.13 and 0.45% Fe are also plotted in fig 5.9. Both the 0.13% and 0.45% samples show a linear resistivity below 4 K, of slopes $- 0.0014$ and $- 0.0052 \mu\Omega\text{cm/K}$ respectively, but below about 2 K the data for the 0.13% alloy deviate clearly from this line, having the character of a $(1 - AT^2)$ dependence. The resistivity per percent of iron in the two samples may again be compared using the quantity $m = (1/C)(d\rho/dT)$, which now has more physical significance as the resistivities are linear in temperature in the region of maximum gradient. The values of m obtained are $- 0.0108$ and $- 0.0116 \mu\Omega\text{cm/K/\%}$ for the 0.13% and 0.45% samples respectively, showing that in spite of a change in the Kondo temperature by a factor of at least 2, the actual magnitude of the scattering effect has only changed by about 10%.

The resistivities of the $(V_{10}Cr_{90})$ based alloys are plotted over the full range of measurement in fig 5.10, and again the subtraction of the phonon contribution yields qualitatively a logarithmic temperature dependence for the impurity effect. In order to test the high temperature results more rigorously, the resistivities of these samples and the two more dilute samples of the $(V_{20}Cr_{80})$ composition were plotted against $\log T$. Figs 5.11 and 5.12 show that a strict

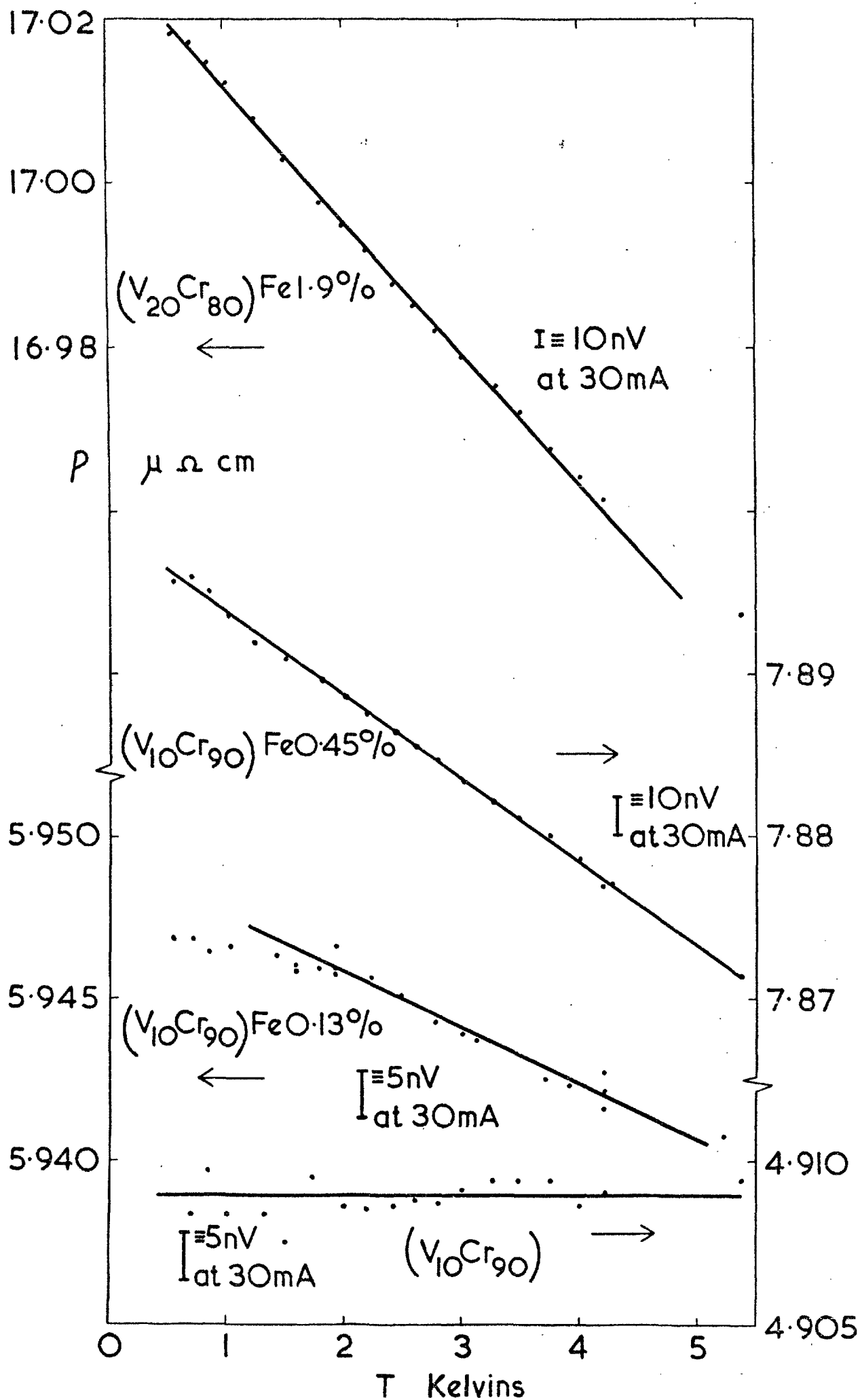


Fig 5.9 Resistivities of some chromium-rich (V-Cr)Fe alloys below 5 K

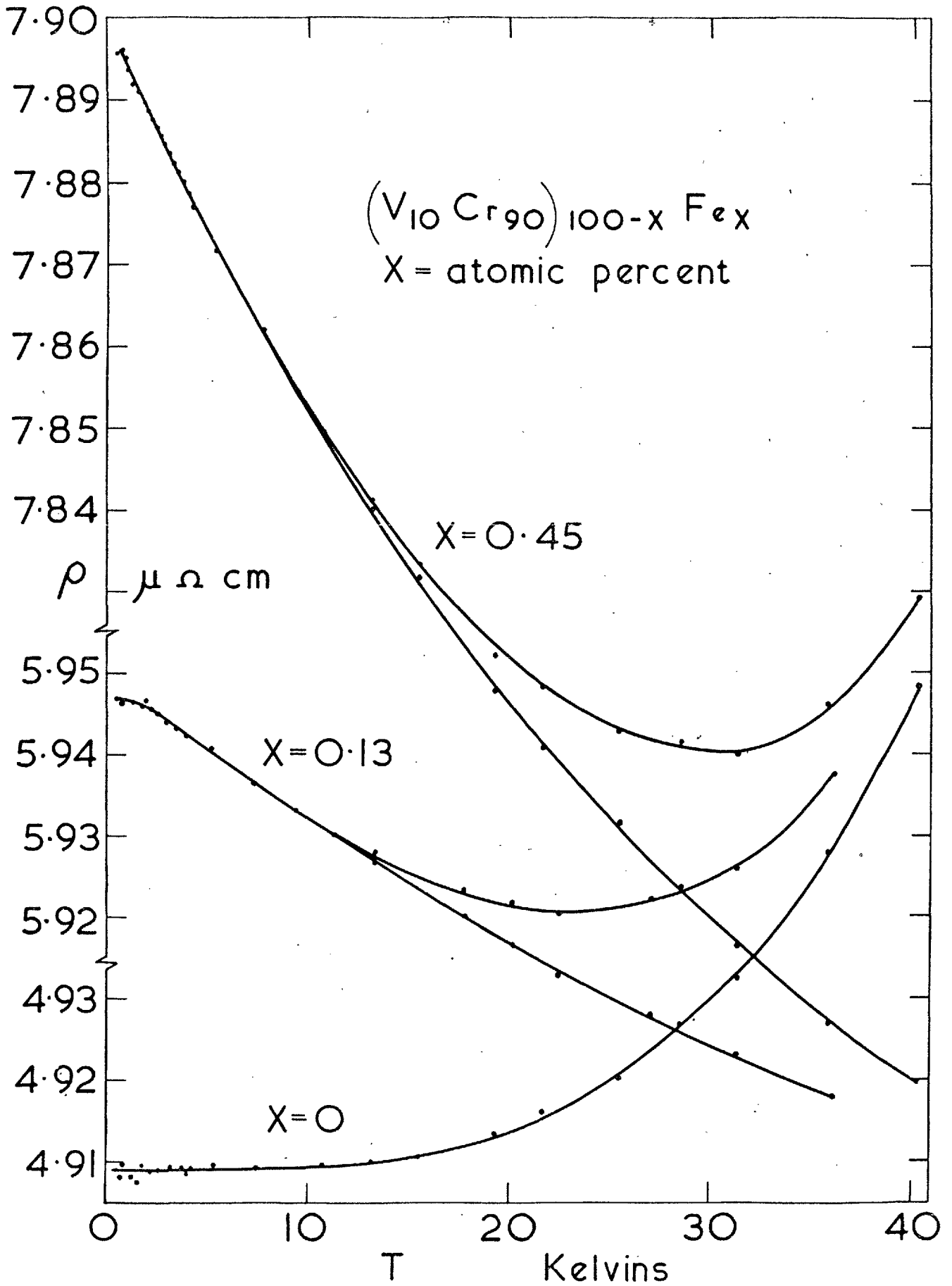


Fig 5.10 Resistivities of alloys of $(V_{10}Cr_{90})$ containing 0, 0.13 and 0.45% iron

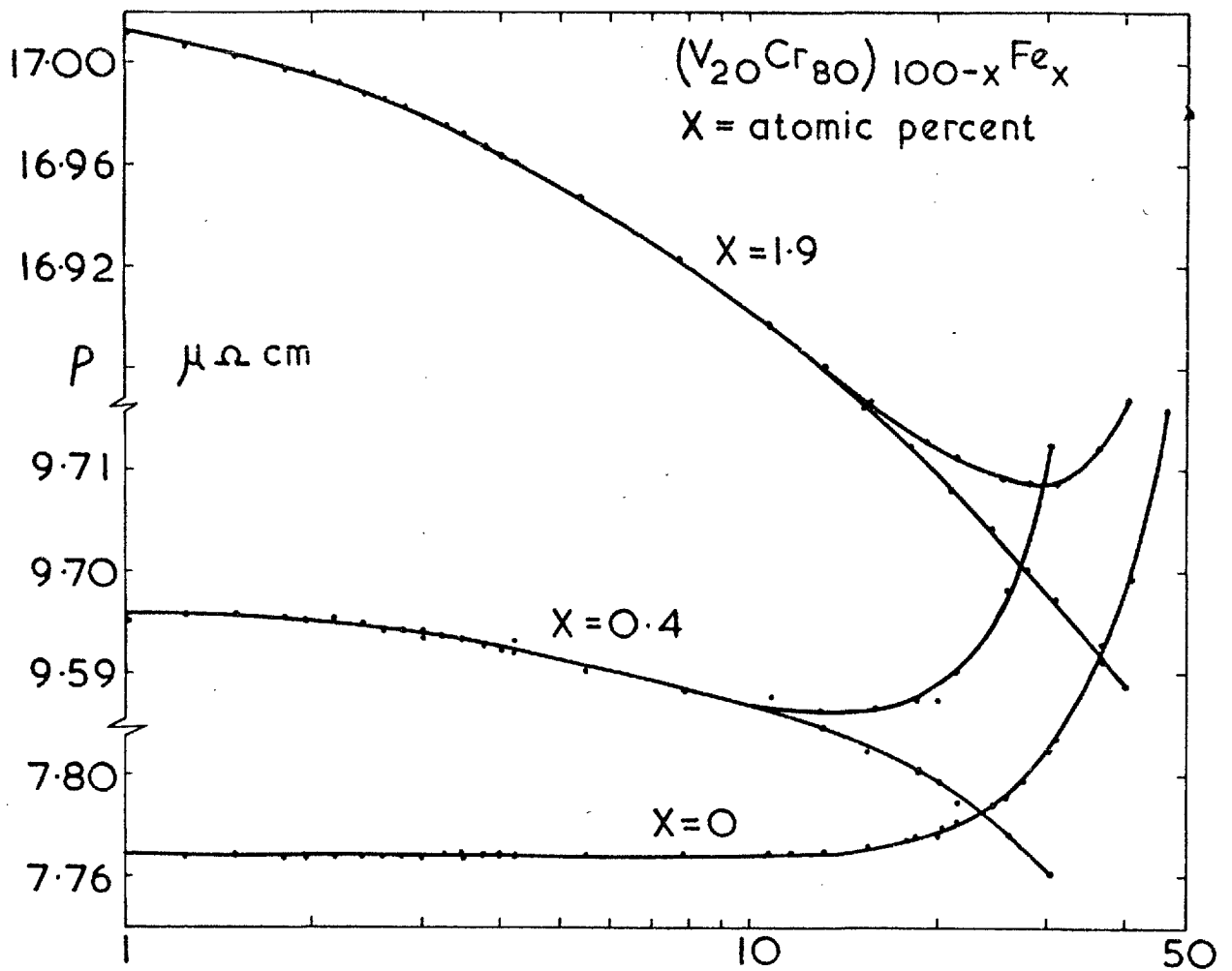


Fig 5.11 Resistivities of alloys of $(V_{20}Cr_{80})$ containing 0, 0.4 and 1.9% iron plotted against $\log T$

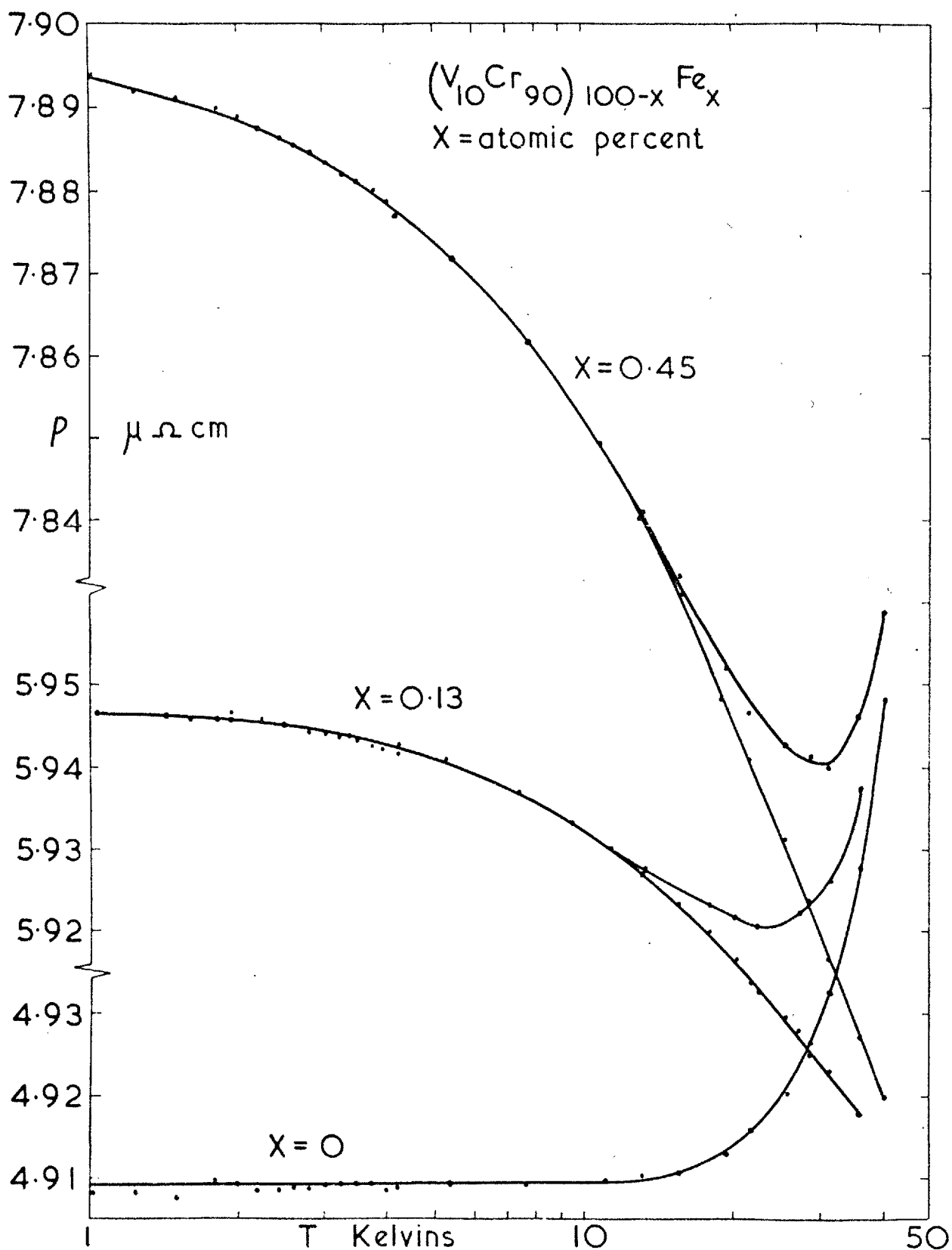


Fig 5.12 Resistivities of alloys of $(V_{10}Cr_{90})$ containing 0, 0.13 and 0.45% iron plotted against $\log T$

logarithmic dependence was not observed in the impurity resistivity of any of these samples though the curvature in the subtractions $(\rho - \rho_{\text{host}})$ for the $(\text{V}_{20} \text{Cr}_{80})$ 1.9% Fe and the $(\text{V}_{10} \text{Cr}_{90})$ Fe 0.45% Fe was fairly weak between 15 K and 40 K. Such curvatures could arise from errors in the absolute resistivities of the alloys and therefore the existence of a $\log T$ term in the resistivities of these alloys, while not confirmed in detail, is strongly suggested. In the more dilute alloys, for which the Kondo temperature is higher, it would seem that the $\log T$ region is not well established in the range of these experiments, and in the $(\text{V}_{20} \text{Cr}_{80})$ 0.4% Fe sample particularly the curvature in the impurity resistivity is still pronounced at 30 K.

5.4 Conclusions

The results of section 5.2 serve to show that 3 d solutes are nonmagnetic in vanadium at low temperatures and the resistivities gave no indication that spin fluctuation effects make a significant contribution to electron scattering up to 77 K. Thus if virtual bound states can be said to exist on the solute atoms, they must be greatly broadened, or if the alloys are better described by the collective band model, then the exchange enhancement factors appropriate to them are small. The discovery of a resistance minimum in the $(\text{V}_{20} \text{Cr}_{80})$ Fe 0.4% alloy showed that there is a virtual bound state associated with an iron atom dissolved in the V-Cr system and that it is magnetised in the chromium-rich alloys where the density of states is low. These results are similar to those obtained for the resistivities of (Nb-Mo) Fe alloys by Sarachik et al. (1964) who found that 1% Fe gave rise to a resistance minimum in host compositions containing more than 60% Mo.

The effect of varying the concentration of iron in chromium-rich V-Cr alloys was investigated and the results may be interpreted in the following way. In the dilute limit where there are no interactions

between solute atoms, the magnetic and electrical properties are those of a Kondo system with a characteristic spin fluctuation, or Kondo, temperature T_K which falls with increasing chromium content. The resistivity is then expected to be proportional to $(1 - AT^2)$ at the lowest temperatures, then to vary as $(1 - BT)$ and above T_K as $(-\log T)$ (Rivier and Zlatic 1972 a). As the iron content is increased, interactions of the RKKY type become important, and at first have the effect of stabilising the magnetic moments. The magnitude of the scattering per iron atom is thereby increased, T_K is reduced and the universal curve of Rivier and Zlatic is shifted to lower temperatures. These effects were observed in the resistivities of both the $(V_{30}Cr_{70})$ and $(V_{20}Cr_{80})$ hosts as the iron content was increased from 0.5% to 2%. In the former the resistance minimum was undetected at 0.5% Fe but was pronounced in the 2% alloy (fig 5.5), while in the latter, fig 5.8 shows that the magnitude of the impurity resistivity was increased substantially more than in proportion with the concentration. In the $(V_{10}Cr_{90})$ system the magnetic moment of an isolated iron atom is much better established, the temperature dependence of the impurity resistivity is large and the Kondo temperature is relatively low. Even so a linear region in the resistivity was observed in the 0.45% Fe sample in the helium range and in the 0.13% sample a clear deviation towards a $(1 - AT^2)$ dependence was detected below 2 K. Interaction effects in the 0.45% sample are therefore found substantially to increase the spin fluctuation lifetime (or depress T_K) but since the amplitude of the fluctuating moment is already large at 0.13% Fe the magnitude of the resistivity per percent of solute is not greatly increased in the 0.45% alloy. By contrast the reduction of the iron content from 1.9% to 0.4% in the $(V_{20}Cr_{80})$ composition is accompanied by such a loss of magnetic moment that the $(1 - AT^2)$ dependence which is probably present at the lowest temperatures (since the linear region

was observed in the 1.9% sample - fig 5.9) is hidden in the scatter of the data plotted in fig 5.6. It is significant that the value of m (the slope of the resistivity per percent of iron in the region of linear temperature dependence) determined for the $V_{10}Cr_{90}$ alloys, $- 0.011 \mu\Omega\text{cm/K/\%}$, is close to the maximum value obtained in the $(V_{20}Cr_{80})$ composition, $- 0.009 \mu\Omega\text{cm/K/\%}$ at 1.9% (fig 5.8).

The second consequence of the interactions between iron atoms is that at a sufficiently low temperature, a transition to magnetic order of the 'spin glass' type should be observed. In the dilute alloys this temperature was outside the range of the present experiments and the onset of ordering was therefore investigated by increasing the iron concentration, thereby increasing the magnitude of the interactions. The results for the $(V_{20}Cr_{80})$ composition with up to 8% Fe showed (figs 5.7 and 5.8) that the effect of the ordering is to reduce the impurity scattering and at a high enough concentration to give rise to a low temperature resistance maximum.

These interaction effects strongly parallel those which were found in Rh Fe and are discussed in chapter 3. Both Rh Fe and chromium-rich $(V-Cr)$ Fe alloys conform to the Rivier-Zlatic theory of the resistivity due to scattering by spin fluctuations, though the sign of the temperature dependences are different. In both systems, as the iron concentration is increased above the dilute limit, the interactions between solute atoms produce a stabilisation of the spin fluctuations and a reduction in the characteristic temperatures. Thus a resistivity proportional to T^2 in the helium range was observed in $(V_{10}Cr_{90})Fe$ and in Rh Fe at an iron concentration of $\sim 0.1\%$, but at 0.5% Fe the spin fluctuation temperature in both cases was reduced so that the T^2 region was depressed to below 0.5 K. The similarity of this effect in the two systems is illustrated by a comparison of figs 3.10 and 5.10. The analogy between the Rh Fe and the $(V-Cr)$ Fe alloys also persists to

to higher iron concentrations. The transition to the magnetic spin glass state in $(V_{20}Cr_{80})$ Fe alloys at 5% and 8% Fe has been detected by the present resistivity measurements, and the measurements of Murani and Coles (1970) particularly of the susceptibility of Rh Fe demonstrate that ordering of the spin glass type also occurs in this system, at temperatures above 2 K for iron concentrations $> 3\%$.

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