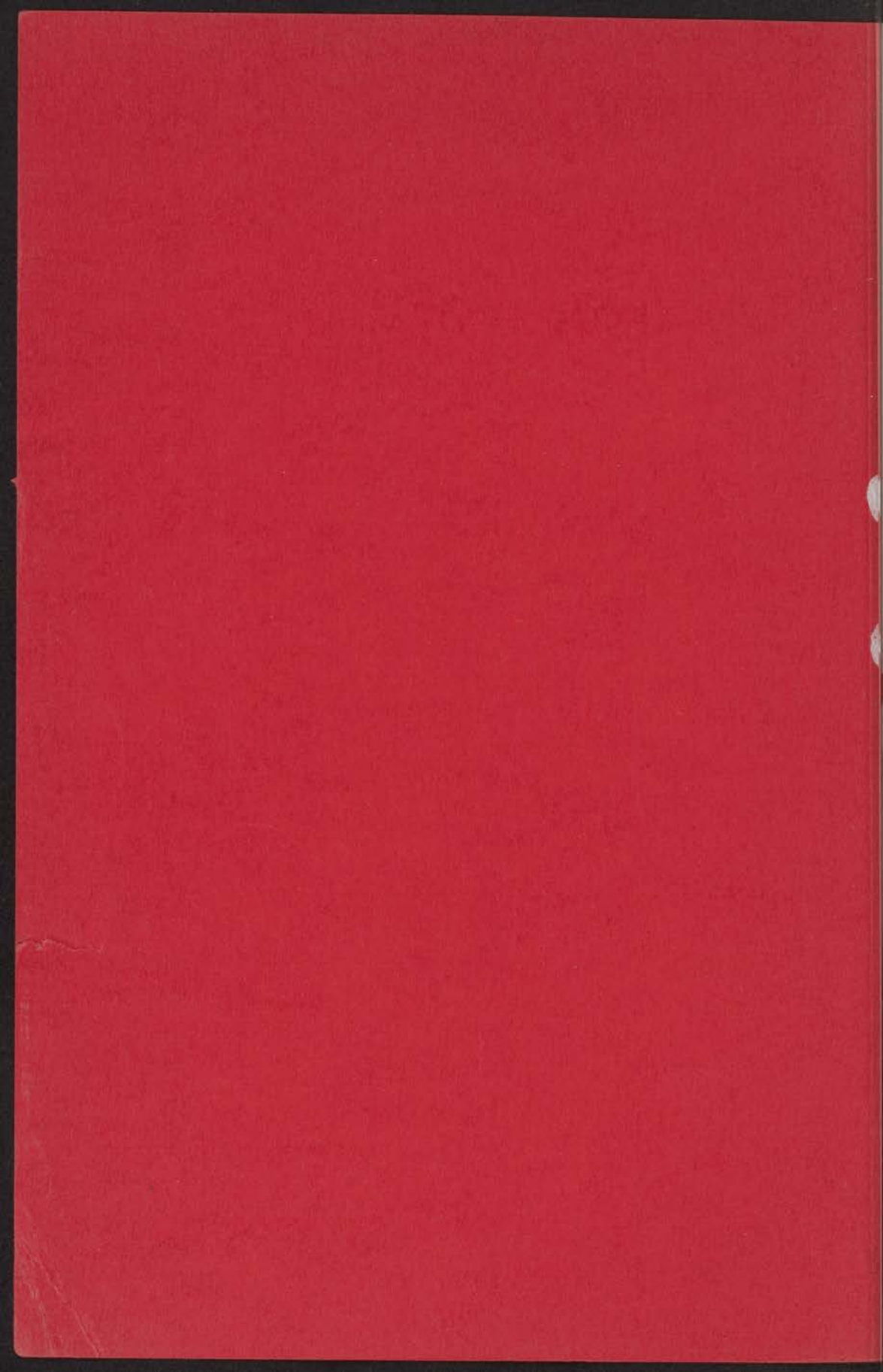


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TOWARD
SIMPLE POWERS
OF T
IN THE
KONDO EFFECT

INSTITUUT LORENTZ
voor theoretische natuurkunde
Houwsteeg 18-Leliden-Nederland

W. M. STAR



- 9 MAART 1971

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kast dissertaties

THE UNIVERSITY OF CHICAGO

PHYSICS DEPARTMENT

PHYSICS DEPARTMENT

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**TOWARD SIMPLE POWERS OF T
IN THE KONDO-EFFECT**

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE WIS-
KUNDE EN NATUURWETENSCHAPPEN AAN DE RIJKSUNI-
VERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR MAGNIFI-
CUS DR. C. SOETEMAN, HOOGLERAAR IN DE FACULTEIT
DER LETTEREN, TEN OVERSTAAN VAN EEN COMMISSIE UIT
DE SENAAAT TE VERDEDIGEN OP WOENSDAG 17 MAART
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Promotor: Prof. dr. C.J. Gorter

Dit proefschrift kwam tot stand onder toezicht van dr. C. van Baarle

Co-referent: dr. G.J. van den Berg

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aan mijn ouders

to my parents



Deze kleine gele bolbloem draagt dezelfde naam als Jun Kondo, de man wiens werk aan het begin staat van een ontwikkeling, waaraan dit proefschrift een bijdrage levert. Dit is één reden om bovenstaande foto op te nemen. De andere reden is dat bloembollen van mijn vader – tulpen om precies te zijn – de financiële basis vormden voor mijn studie.

This little yellow bulb-flower happens to bear the same name as Jun Kondo, the man whose work stands at the beginning of a development, to which this thesis makes a contribution. This is one reason to include the picture. The other reason is that my father's flower-bulbs – tulips actually – provided for the financial basis of my study.

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CHAPTER I

HISTORICAL INTRODUCTION; MISCELLANEOUS REMARKS

I.1. Definition of history; review of reviews

Within the context of this thesis history begins — and prehistory ends — in 1964. In that year a paper by J. Kondo was published, entitled 'Resistance minimum in dilute magnetic alloys'¹), which now marks the beginning of a new era in the understanding of magnetic impurities in nonmagnetic metals. Kondo showed for the first time theoretically that at low temperatures the electrical resistivity of a metal containing noninteracting paramagnetic impurities might increase with decreasing temperature, due to the so-called s-d exchange interaction, after the phonon scattering of electrons has died out sufficiently. Experimentally the resistance-minimum phenomenon had been known for more than thirty years, but no satisfactory explanation was given. It had been observed for the first time by Meissner et al.²) in 'pure' Mg, Co, Mo, Pd and Te and was attributed to impurities. These authors did not seem to be surprised and paid no more attention to it. A few years later the effect was found in 'pure' gold³) and the temperature of the resistivity minimum appeared to decrease with the residual resistivity i.e. with the concentration of impurities. It was pointed out by one of the authors many years later⁴) that probably iron had been the main contaminant. But it was by no means clear from the outset that only magnetic impurities would cause a resistance minimum. Even in 1960⁵) some people were still considering the possibility that nonmagnetic atoms like Sn, In, Ge, or even grain boundaries would do, although experimental evidence pointed toward the contrary^{6,7}). Even a few years after the appearance of Kondo's¹) paper this possibility was again considered theoretically⁶). In fact, there exists some recent experimental evidence of resistivity minima in concentrated palladium alloys which are certainly not caused by magnetic atoms. We will discuss them briefly in chapter IV.

In the semiclassical transport theory for electrons in metals by Sommerfeld and Bethe^{7,5}) — still the only theory useful for practical purposes — there are two possibilities to obtain a temperature-dependent resistivity caused by impurities.

Firstly, if the impurities are nonmagnetic, there is potential scattering only. A strongly energy- and wave-vector-dependent scattering cross-section is not expected and one cannot derive a temperature-dependent resistivity, unless a very anomalous Fermi-surface is assumed. Around 1960, when some experimentalists believed they had observed resistivity anomalies produced by nonmagnetic impurities, the first experimental Fermi-surface studies were carried out. It was discovered that the Fermi surface of copper touches the zone boundary in some directions. Following a suggestion by Cohen and Heine, that the addition of impurities would distort the Fermi-surface, causing it to

pull away from the zone boundary and tend to a sphere, Ziman⁸⁾ performed a calculation for copper. He concluded that there should be an effect on resistance and thermopower when the Fermi-surface leaves the zone boundary. The electrical resistivity would show a minimum, but the thermopower anomaly would be positive. This last conclusion was in disagreement with experiment since in general a large negative thermopower associated with a resistance minimum had been observed.

Secondly, if the impurities are magnetic there will be exchange scattering in addition to potential scattering, and a strongly energy-dependent electron-scattering cross-section might be expected. Calculations had been performed before Kondo's¹⁾ publication, but not beyond the first order Born approximation. In that approximation isolated magnetic atoms would not cause a resistance minimum. But scattering of electrons by magnetic ion pairs would indeed produce the desired effect. It is interesting to quote T. van Peski - Tinbergen in a paper⁹⁾ which appeared one year before Kondo's: 'Obviously the pair-model does not allow a quantitative comparison between theory and experiment. It is believed, however, that the pair-model exhibits the essential features of the actual situation in a qualitative way'. Admittedly, this theory not only accounts for the resistance minimum, but also for the maximum which had been observed at temperatures below the minimum if the impurity concentration was increased¹⁰⁾. The model had one serious drawback, however, in that experiments had shown the resistivity curves at low temperatures and small impurity concentrations to scale more or less with concentration. On the basis of the pair-model one would rather expect the impurity contribution to the resistivity to be proportional to the square of the concentration.

We will not continue to describe prehistory. The subject which we are dealing with in this thesis has been reviewed continually in recent years. Fairly comprehensive articles are available covering experimental as well as theoretical history up to 1969. Therefore, before proceeding, we will mention some of them.

1. Almost all the work which was of any relevance to the problem of magnetic impurities in non-magnetic hosts has been quoted by van den Berg¹¹⁾. This article appeared quite accidentally in 1964 and may be considered to contain all the prehistory. It is mainly an experimental review, but it also refers to most of the then existing theories.
2. Another experimental review was written by Daybell and Steyert¹²⁾ after four years of theoretical developments since Kondo. This paper mainly reconsiders the old experimental data to show that the 'Kondo-temperature' (see section I.3) may vary over several decades of temperature.
3. The paper by Heeger¹³⁾ is not so much an experimental review like refs.¹¹⁾ and¹²⁾ are as it is a critical discussion of some of the available data with regard to existing theories, and with special emphasis on the very low-temperature properties ($T < \text{'Kondo-temperature'}$, see section I.3) and the ground state of the magnetic impurity in the metal. As regards electron transport properties and, less extensively, specific heat and susceptibility we will in the following chapters take up the thread where Heeger left it. Heeger's paper already contains some references to

- prepublications of the work which we will describe and which may clarify some of the inconsistencies noted by Heeger and will show how the experimental situation at this moment differs from the picture given by him.
4. The short paper by van Dam and van den Berg¹⁴) which appeared recently is, within its scope, the most up-to-date review, especially as regards the experiments carried out in the metals group of the Kamerlingh Onnes Laboratory.
 5. A number of theoretical achievements has been reviewed by Bailyn¹⁵). His paper includes Kondo's theory and its first follow-up, but not the big boom of theoretical work after mid-1965.
 6. Kondo's review article¹⁶) mainly discusses the s-d exchange model used in his already classic paper¹), the foundations of the model and the development of the theory up to 1969, the attempts to remove divergencies (see section I.3) and the problem of the ground-state.
 7. Fischer's discussion¹⁷) is very much along the same lines as Kondo's. He also reviews the results obtained with the s-d model. He does not, like Kondo, include a discussion of the formation of local moments, but adds a short discussion of recent experimental results.
 8. Finally we want to mention a few articles⁹³) by Abrikosov and Anderson, which are of interest to those who like to see the physical ideas translated into words, instead of being concealed in mathematics.

Most of the history which is of importance for this thesis may be found in the articles mentioned above. Yet we want to give some more historical introduction to the work to be described in the following chapters. We have actively followed the developments since 1964 and later participated in them. The history which we will describe will therefore be the history as we have personally experienced it and as it led us to our experiments and their interpretation.

I.2. A step forward by Kondo

Before starting his calculation, Kondo pointed out two experimental observations. Firstly, he noticed that at small concentrations the temperature-dependent impurity contribution to the resistivity was reasonably well proportional to the concentration. Secondly he observed that the occurrence of a resistance minimum was generally associated with the existence of a magnetic moment on the impurity atom.

In the preceding section we remarked that a few years earlier people were still considering the possibility that non-magnetic impurities also would cause a resistance minimum. But evidence was growing that the impurity atom should be magnetic. The work of Sarachik¹⁸) on the resistivity of Fe dissolved in Nb-Mo and Mo-Re alloys showed an intimate connection between the magnetism of the Fe-atoms and the occurrence of a minimum.

We also remarked in the preceding section that no anomalous energy dependence of the electron-scattering cross-section had been obtained by calculations in the first order Born approximation. Thus Kondo went to second order, and with success. He used a Hamiltonian containing a free-electron term

and a perturbation term, reading (if only one impurity at the origin is considered):

$$H_{sd} = - (J/N) \sum_{k,k'} [(a_{k+}^* + a_{k'}^* - a_{k-}^* - a_{k'}^*) S_z + \\ + a_{k+}^* + a_{k'}^* - S_- + a_{k-}^* - a_{k'}^* + S_+] \quad (1.1)$$

which is essentially the second-quantized form of the Hamiltonian $H = -J S \cdot s$. In formula (1.1) all symbols have the usual meaning i.e. a_{k+}^* is a construction operator for an electron in a state with wave vector k and spin up. S and s are the spin operators of the impurity atom and a conduction electron, respectively. $S_{\pm} = S_x \pm i S_y$. The exchange integral is taken to be independent of k and k' . N is the total number of atoms. Kondo did not take into account potential scattering. Inclusion of potential scattering is important if one wants to calculate the thermopower for example¹⁹), but in Kondo's approximation it is not essential for the resistivity.

For the electronic relaxation-time τ_k the following results was obtained:

$$\tau_k^{-1} = [3 \pi^2 z J^2 S (S + 1) c / E_F h] [1 + 4 J g(E_k)] \quad (1.2)$$

E_F is the Fermi energy, E_k the energy of an electron with wave vector k , c is the impurity concentration, z is the number of conduction electrons per host-atom and h is Planck's constant. The function $g(E_k)$ is equal to

$$g(E_k) = \int_{\text{bandwidth}} \frac{\rho(E) f(E)}{E - E_k} dE \quad (1.3)$$

$\rho(E)$ is the electronic density of states per spin, $f(E)$ the Fermi-Dirac distribution function. This last function is almost a step-function if $k_B T \ll E_F$, which is certainly the case below room temperature in most metals. Thus $g(E_k)$ is a strongly varying function of E_k if $E_k \approx E_F$. $g(E_k)$ provides the strong energy-dependence of τ_k , necessary to obtain a temperature-dependent resistivity. At $T = 0$ it equals $\rho(E_F) \ln(|E - E_F|/E_F)$ which diverges at the Fermi energy.

The electrical conductivity is calculated in the standard way²⁰) and the result for the resistivity is:

$$\rho_{\text{res}} = c \rho_M [1 + (3zJ/E_F) \ln T] \quad (1.4)$$

The value of

$$\rho_M = 3\pi^2 m J^2 S(S + 1) V / N e^2 h E_F \quad (1.5)$$

is approximately $23(J/E_F)^2 S(S + 1) \mu\Omega \text{ cm/at.}\%$ for an impurity in copper (e is the charge of the electron, m its mass, V the volume of the metal).

A behaviour like that predicted by formula (1.4) had been observed already in 1953 by Croft et al.²¹). Within the limited precision of their measurements a fit was possible from 0.007 K up to 4 K. As an

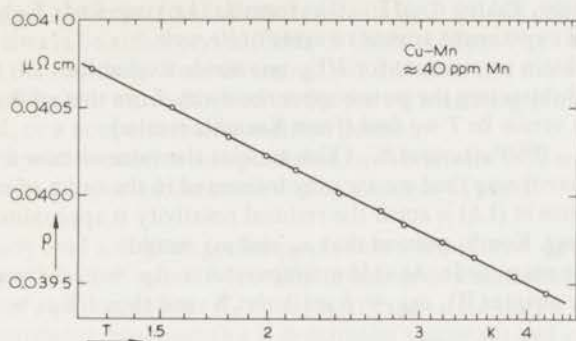


fig. 1.1 Electrical resistivity of a Cu-Mn dilute alloy vs. $\log T$. The wire was not annealed, which explains the rather high resistivity; $d\rho/d \ln T = -1.04 \times 10^{-9} \Omega \text{ cm}$.

example we show in fig. 1.1 the resistivity of a Cu-Mn dilute alloy. The temperature region is limited (the $\ln T$ may apply over far more than one decade in T), but the fit is quite good. Using formulae (1.4) and (1.5) one finds $J/E_F \approx -0.078$ if $S = \frac{5}{2}$, thus $J \approx -0.55 \text{ eV}$ if $E_F = 7 \text{ eV}$. Monod²²) finds $|J| = 0.4 \text{ eV}$ from magnetoresistance measurements.

It is clear that $|J/E_F|$ has to be much smaller than unity for Kondo's calculation to be applicable. This condition is reasonably well satisfied for Mn in Cu. Furthermore, an antiferromagnetic coupling between the conduction electrons and the magnetic impurity is necessary to obtain a resistivity which increases with decreasing temperature.

Kondo¹) compared his result with experiments on three systems: iron in copper, gold and rhodium, respectively. We will recall the discussion of Cu-Fe, because this system plays an important role in the following sections. The Cu-Fe alloy has the advantage that the iron contribution to the resistivity is proportional to its concentration in a fairly wide range of concentrations.

Empirically, the resistivity of dilute Cu-Fe alloys may be written as

$$\rho_{\text{res}} = c\rho_p + c\rho_M [1 + (3Jz/E_F) \ln T] + AT^5 \quad (1.6)$$

In this expression ρ_p contains all the temperature-independent impurity resistivity not contained in ρ_M . AT^5 represents the copper-lattice resistivity. It is important to notice that the lattice-resistivity of Cu is indeed very precisely proportional to T^5 up to 20 K. This is not the case with Al, for example, which has a higher Debye-temperature than copper.

Pearson, in an extensive investigation of resistance minima²³), observed* $T_{\text{min}} \sim c^{1/5.2}$, and Knook²⁴) in a similar investigation found

* Strangely enough in the same paper Pearson reported that Cu-Bi alloys would also show a resistance minimum with $T_{\text{min}} \sim c^{1/4.8}$. As Bi is nonmagnetic one would rather expect a constant T_{min} (due to magnetic impurities in the pure Cu) or a T_{min} decreasing with Bi-concentration if positive deviations from Matthiessen's rule occur.

$T_{\min} \sim c^{1/5.3}$ for the variation of the temperature of the minimum in Cu-Fe with concentration. Taking $d\rho/dT = 0$ in formula (1.6) one finds $T_{\min} \sim c^{1/5}$. Thus theory and experiment appear to agree quite well.

In order to obtain an estimate for J/E_F one needs a value for $c \rho_M (3J/E_F)$. Subtracting the pure-copper resistivity from that of the alloy and plotting $\Delta\rho$ versus $\ln T$ we find (from Kondo's results) $\rho_M (3J/E_F) = -0.60 \mu\Omega \text{ cm/at.}\%$. (This is twice the value obtained by Kondo in a slightly different way, but we are only interested in the order of magnitude). As the $\ln T$ term in (1.6) is small the residual resistivity is approximately equal to $\rho_P + \rho_M$. Kondo guessed that ρ_P and ρ_M would be of comparable magnitude. As at low temperatures $\Delta\rho \approx 12 \mu\Omega \text{ cm/at.}\%$ for Fe in Cu (see chapter II), $\rho_M \approx 6 \mu\Omega \text{ cm/at.}\%$ and thus $J/E_F \approx -0.03$ i.e. $J \approx -0.2 \text{ eV}$.

In both systems which we discussed – and in others discussed by Kondo – the situation seems rather satisfactory: the experimental results for the resistivity can be explained, and the values deduced for J/E_F make sure that terms higher than second order in Born's approximation may be neglected.

Besides, also the negative magnetoresistance and the resistance maximum, which appeared in various dilute magnetic alloys at temperatures below the minimum, could readily be accounted for. Kondo, in his calculation, assumes the impurity spins to be completely free, except for the s-d exchange interaction. If an external magnetic field is applied spin-flip scattering, i.e. the $\ln T$ -term, is suppressed, causing the resistivity to drop below its value at $H = 0$. But there are also internal magnetic fields acting on the impurities, due to long-range polarization of the conduction electrons by surrounding impurities. These internal fields increase in strength with increasing impurity concentration and a resistance maximum will occur if for a sufficiently large fraction of atoms the thermal energy becomes smaller than the Zeeman energy with decreasing temperature. Actually, the resistance maximum and the negative magnetoresistance had in principle been explained by Yosida²⁵) long before Kondo's publication.

As to the Cu-Fe system we should make a remark which makes the situation look less satisfactory. If we use $J \approx -0.2 \text{ eV}$ to compute ρ_M with expression (1.5) we obtain $\rho_M = 0.07 \mu\Omega \text{ cm/at.}\%$, which is quite small compared to the estimate made above. On the other hand, if we use the experimental value of $d\rho/d\ln T = -0.6 \mu\Omega \text{ cm/at.}\%$, (1.5) and $S = \frac{3}{2}$ ²⁶) we find $J/E_F \approx -0.13$ and $J \approx -0.9 \text{ eV}$, which is not so small anymore. We will return to this inconsistency in section 1.4.

1.3. The follow-up

Experimentally the resistance-minimum problem seemed to be solved in principle, but theoretically the real problems now emerged. The scattering cross-section calculated by Kondo diverges for $E \rightarrow E_F$ and higher orders in the Born approximation diverge even more strongly. As the maximum possible partial cross-section equals $\sigma_{\ell} = (4\pi/k_F^2) (2\ell + 1)$ and for transition-metal

impurities probably only the $\ell = 2$ phase-shift will differ appreciably from zero, one does not expect an infinite resistivity at $T = 0$. Of course, in practice there will always be either crystal fields or fields produced by other impurities to prevent the resistivity from diverging, but that does not solve the fundamental difficulty. Thus the whole Born series for the s-d scattering problem had to be considered, or a nonperturbative method devised.

The first such treatment was published by Abrikosov^{27,28}) and from that time theorists dominated the scene during a couple of years.

Abrikosov used a diagram technique to sum a set of most divergent terms from the perturbation series. According to his result a scattering resonance would occur at a temperature $T_C \approx (E_F/k_B) \exp(-1/|J| \rho_1)$ if $J < 0$, thus in the case of a resistance minimum (k_B is Boltzmann's constant and ρ_1 is the electronic density of states per spin per host atom at the Fermi surface). Kondo's result was reproduced far above T_C . At T_C the resistivity would pass through a maximum and would go to zero as $(\ln T)^2$ for $T \rightarrow 0$. For $J > 0$ the resistivity would equally go to zero, but without going through a maximum and no resonance occurs.

At about the same time a similar result was obtained by Suhl²⁹) using a different method. It became clear that the divergence in Kondo's theory would not survive in an exact theory. It appeared somewhat strange that the resistivity due to exchange interaction would go to zero at $T = 0$. Apparently the methods of Abrikosov and Suhl were not yet well enough developed to provide correct results below T_C . Later this problem was solved by Suhl and Wong³⁰). In the case of a resistance minimum the resistance increases monotonically with decreasing temperature and attains a finite value at $T = 0$. This was also the conclusion of Nagaoka³¹), the third author who contributed to the immediate follow-up after Kondo's publication. We will dwell upon Nagaoka's work for a while because his method and physical ideas played an important role in later thinking and because he provided a useful expression for the resistivity, which is what experimentalists like.

Nagaoka used a Green's function method which had been applied earlier to the case of superconductivity by Zubarev. Nagaoka obtained a set of coupled equations of motion, which he decoupled in lowest nontrivial order by replacing certain statistical averages of products of operators by products of their averages. By this method Zubarev had obtained the results of Bardeen, Cooper and Schrieffer for a superconductor. Some of the notions of superconductivity will reappear in a form transposed to the s-d exchange problem in what follows.

Nagaoka's high-temperature perturbational solution reproduced Kondo's result. However, the inverse lifetime of the conduction electrons became negative for $E \rightarrow E_F$ at a critical temperature $T_C \approx (E_F/k_B) \exp(-1/|J| \rho_1)$ i.e. the same T_C as found by Abrikosov and by Suhl. The expression for T_C becomes identical to the expression for the transition temperature of a superconductor if E_F/k_B is replaced by the Debye-temperature and J by the electron-phonon interaction parameter.

From now on T_C will be called the Kondo temperature T_K , and the resistance-minimum phenomenon will be called the Kondo-effect. This is the common nomenclature since 1965/66.

For temperatures below T_K Nagaoka devised a selfconsistent solution, and

for the resistivity he obtained if $T \ll \Delta$ and $S = \frac{1}{2}$:

$$\rho_{\text{res}} = \frac{m}{ne^2} \frac{c}{\pi \rho_1 \hbar} \left[1 + \frac{\pi^2}{3} \left(\frac{T}{\Delta} \right)^2 \right]^{-1} \quad (1.7)^*$$

where

$$\Delta = \Delta_0 \left[1 - (\pi^2/6)(T/\Delta_0)^2 \right] \text{ and } T_K = 1.14 \Delta_0 \quad (1.8)$$

The resistivity thus attains a maximum value at $T = 0$, which corresponds to the maximum partial cross-section $4\pi/k_F^2$ for a partial wave with $\ell = 0$

There does not occur a sharp transition at T_K , nor is there an energy gap like in superconductivity. There rather occurs a gradual transition into what seems to be a low-temperature quasibound spin state. Nagaoka calculated a long range spin polarization antiparallel to the localised spin, which would tend to reduce the effective magnitude of the localised spin and might completely compensate it at $T = 0$. The quasibound-spin state is reminiscent of – but certainly not similar to – the Cooper pair in a superconductor. The range of the antiparallel spinpolarization would be of order $(\hbar v_F/k_B T_K)$, later called coherence length by Heeger, like in superconductivity.

1.4. Nagaoka's theory and the Copper–Iron problem

Not long after the publication of Nagaoka's³¹⁾ paper we became aware of the qualitative similarity between the resistivity-versus-temperature curve of dilute Cu-Fe alloys and the behaviour as predicted by Nagaoka. That is to say, in going towards temperatures below 3 K the slope $-d\rho/dT$ appeared to decrease, even for small iron concentrations (see fig. 1.5).

In fact it was already known for some time that the behaviour of Cu-Fe was somewhat different from other dilute alloy systems. Martin³²⁾ once roughly divided all dilute magnetic alloys into two classes, according to the behaviour of the specific-heat anomaly, which was generally observed in connection with the resistivity-anomaly. The first class would contain systems for which the temperature of the maximum in the specific-heat hump is independent of impurity-concentration. In the resistivity-versus-temperature curve of these systems no maximum had been observed. The second class would contain alloys where the temperature of the specific-heat maximum depends on concentration, and a resistivity-maximum is observed with increasing concentration. The first class had only two members: Cu-Fe and Cu-Cr, the second alloy being a borderline case.

Measurements of the Mössbauer-effect of ^{57}Fe in Cu were published³³⁾ at about the same time as Nagaoka's paper and revealed a strong deviation from paramagnetic behaviour, which could not be accounted for.

The decrease of $-d\rho/dT$ with temperature in Cu-Fe had frequently been

* This original result is actually in error. The resistivity at $T = 0$ should be multiplied by 2 and then equals $3.8 \mu\Omega \text{cm/at.}\%$ for copper as a host.

regarded as the onset of a resistance maximum. Measurements down to below 0.1 K had been performed by White³⁴) and by Dugdale and MacDonald³⁵) on Cu-Fe (0.056 at. % Fe). The most precise results, obtained by the latter authors, revealed a temperature-independent resistivity below 0.5 K.

A resistivity-curve which tends to flatten at low temperatures may always be fitted to a parabola in a limited temperature-region. We again used Knook's²⁴) results for Cu-Fe, plotted the resistivity versus T^2 and obtained a slope at the lowest temperatures ($T > 1.2$ K) which was reasonably well proportional to concentration: $d\rho/dT^2 = -0.0268 \mu\Omega \text{ cm/K}^2 \text{ at. \%}$. With formula (1.7) one then obtains $\Delta = 22$ K. This value is relatively high, in view of the fact that usually resistivity minima were not observed far above 20 K*. But a high value of T_K was not a priori impossible, as a small change in $J\rho$, which occurs in the exponent of the expression for T_K (section 1.3), may cause an enormous shift of T_K . Using the expression $\Delta \approx T_K \approx (E_F/k_B) \exp(-1/|J|\rho)$ an estimate for $J/E_F \approx \frac{4}{3} J\rho_1 \approx 0.11$ may be obtained. So $J \approx 0.8$ eV. These values are in good agreement with the estimates at the end of section 1.2. Unfortunately we noticed only a long time later that Kondo's estimate of ρ_M and thus of J was a little confusing. For the moment we were left with an inconsistent situation: the observed concentration-dependence of T_{\min} ($\sim c^{1/5}$) for Cu-Fe, together with the lattice resistivity being proportional to T^5 , supported Kondo's $\ln T$ -dependence, as did Kondo's estimate of J . Therefore Nagaoka's theory was apparently not applicable because Kondo's $\ln T$ would only be valid for $T \gg T_K$ and we estimated $T_K \approx 22$ K. On the other hand the low-temperature flattening of the resistivity curve occurred already at small Fe-concentrations and did not change appreciably up to 0.1 at. % Fe. But since it was not yet certain that Nagaoka's treatment of the Kondo effect had produced the correct result, we concluded that Cu-Fe was a very complicated system. This was anyway true from the metallurgical point of view.

An anomalously large thermoelectric power had generally been observed to be associated with the Kondo effect. A typical value is $S = -15 \mu\text{V/K}$ at 10 K for Cu-Fe. We were performing thermopower-measurements on dilute magnetic alloys and decided, in view of the above discussion, to measure also the Peltier-coefficient π^* . On quite general grounds the relation $\pi = TS$ may be derived³⁶). But since the Cu-Fe system looked very complicated and π had never been measured at liquid Helium temperatures, the experiment seemed justified. From fig. 1.2 it may be concluded that with respect to thermodynamics of irreversible processes Cu-Fe behaves quite normally.

Another interesting transport property is the thermal conductivity. In particular the Lorenz-number, which relates the thermal conductivity λ to the electrical conductivity σ by $L = \frac{\lambda}{\sigma T}$, is of fundamental importance. If elastic impurity scattering of electrons dominates, L should be equal to the Sommerfeld value $L_0 = (\pi^2/3)(k_B/e)^2$, independent of the temperature. The physical reason for this law is that the large-angle impurity scattering affects the

* With the exception of Au-V, which at that time was not considered to be a dilute magnetic alloy. Other systems with a high T_K were discovered later.

* We omit experimental details, as this experiment does not play an important role in the following discussions.

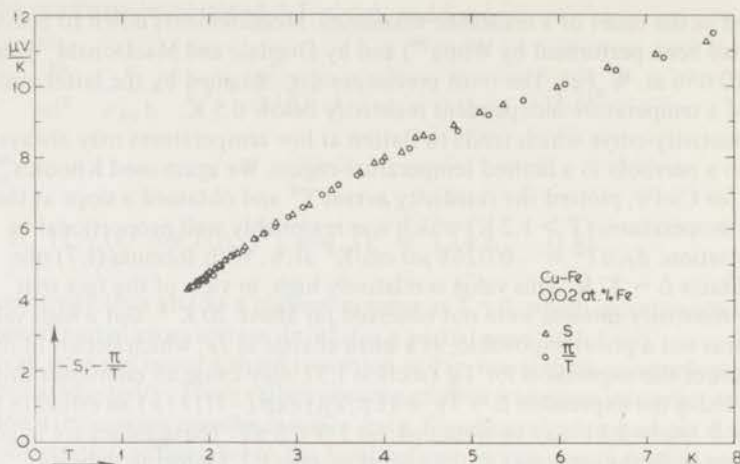


fig. 1.2 Thermopower and Peltier-coefficient of Cu-Fe. The difference between S and π/T is not larger than the error in the measurements, i.e. 3%.

thermal and the electrical conductivities in the same way. If also small- (or large-) angle inelastic scattering occurs the thermal conductivity may be reduced, while the electrical conductivity is not (or less) affected. This may result in a decrease of L below the Sommerfeld value, although at $T = 0$ L should again be equal to L_0 . We were thinking that Cu-Fe might be exhibiting some very peculiar type of magnetic ordering and that measurements of the Lorenz-number might reveal something of it. A preliminary experiment showed that the Lorenz-number was temperature-dependent indeed. The measurements of the Lorenz-number were not completed however, until more than two years later and the interpretation of the results then differed appreciably from the ideas given above (see chapter III).

We interrupted the Lorenz-number measurements when a letter was published by Daybell and Steyert³⁷⁾ who suggested that indeed Nagaoka's quasibound state would be formed by conduction-electron spins about iron impurities in copper. Initially we did not believe this, in view of the fact that Kondo's expression (I.6) appeared to describe the experimental results on Cu-Fe quite well around T_{\min} so that the Kondo-temperature should be lower than 1 K. We were not alone^{38,37)}. We then tried to demonstrate magnetic ordering effects by resistivity measurements. It had been observed by Knook^{24,39)} that addition of Sn to Cu-Fe alloys tended to increase both the depth of the resistance-minimum and the temperature at which it occurs. When Fe-Fe interactions were present these effects could readily be explained. Interactions between magnetic impurities are thought to take place via spin-polarized conduction-electrons. If a sufficient number of nonmagnetic impurities is present these spin-polarizations may be damped and interactions be reduced^{40,41)}. We therefore repeated Knook's experiments, taking Ge instead of Sn (0.002 at. % Fe, max. 0.2 at. % Ge). We found no significant effects.

In another experiment we measured the resistivity of a Cu-Mn, a Cu-Fe and a Cu-Mn-Fe alloy containing 50 ppm Mn and/or Fe. These alloys were prepared

by melting together equal amounts of Cu-100 ppm Mn and Cu-100 ppm Fe either with each other or with pure Cu. The resistivity of Cu-Mn has a logarithmic temperature-dependence (section 1.2) thus a negative curvature on a linear temperature-scale. In Cu-Fe the resistivity curve flattens with decreasing temperature and thus has a positive curvature (fig. 1.5). If Fe-atoms in Cu would strongly polarize the conduction-electrons this would cause magnetic fields on the Mn-atoms. The increase in the resistivity of the Cu-Mn-Fe alloy with decreasing temperature should then be appreciably smaller than the increase in the sum of the Cu-Fe and Cu-Mn resistivities. We observed that the increases were almost equal. So we had not succeeded in demonstrating any kind of peculiar magnetic ordering in Cu-Fe. At about the same time we noticed the confusing estimate of J (section 1.2). We also discovered large deviations from the so called Matthiessen's rule to occur in dilute Cu alloys. Generally, in analyses of electrical-resistivity data, it has been loosely assumed that 'deviations from Matthiessen's rule are small'. We analysed resistivity measurements by Knook²⁴⁾ on Cu-Sn. In fig. 1.3 we show the coefficient A of the phonon-resistivity obtained from the fit $\rho = \rho_0 + AT^5$. A is seen to increase strongly, in particular at the lower concentrations. In fact, for pure copper we always observed A to decrease with the residual resistivity. It is an interesting question to investigate

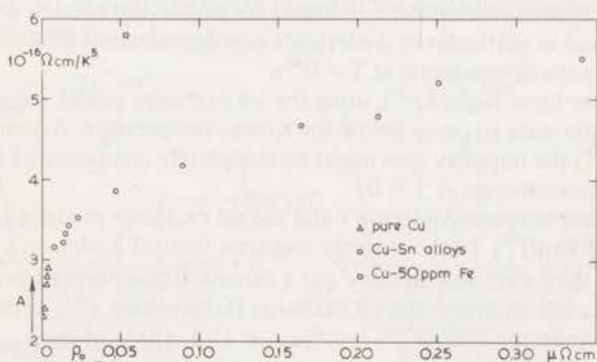


fig. 1.3 Coefficient A of lattice resistivity AT^5 versus residual resistivity ρ_0 of pure Cu and Cu-Sn dilute alloys. See section II.5 for the Cu-Fe point.

whether A will continue to decrease, or whether a definite value for A may be obtained for 'really pure' copper. Lengeler et al.⁴²⁾ have recently published extensive investigations on deviations from Matthiessen's rule in copper and its dilute (non-magnetic) alloys. They did not try to account for the strong variations of A at small residual resistivities however and as far as we know an explanation of them has never been given by anybody else. But this problem is outside the scope of the present discussion. The conclusion which we want to draw is that since A in (1.6) depends on c the observation of $T_{\min} \sim c^{1/5}$ in dilute Cu-Fe is quite accidental and does not constitute a proof of a $\ln T$ -dependence for the resistivity of Fe-impurities in copper, as was assumed in section 1.2.

1.5. A lecture by Schrieffer

It is quite remarkable that not until two years after the appearance of Nagaoka's paper³¹⁾ the first dilute alloy which would behave according to his theory, was proposed in public. It was Cu-Fe, being suggested by Daybell and Steyert³⁷⁾, as we already remarked in the preceding section. A reasonable fit of Nagaoka's expression to their resistivity-results appeared to be possible with $T_K = 16$ K, being of the same order of magnitude as our estimate in section 1.3. Susceptibility measurements revealed a marked decrease of the effective Fe-moment below T_K , in agreement with Nagaoka's suggestion.

A lecture by Schrieffer⁴³⁾ probably had made experimentalists aware of the possibility that and the conditions under which dilute alloy systems with a high Kondo temperature might be found. The physical content of Schrieffer's paper seems to have been put forward already one year earlier by Anderson⁴⁴⁾ but that talk was published by abstract only. The ideas were not accessible to the general public before Schrieffer's publication *).

The Hartree-Fock solution of Anderson's model⁴⁶⁾ for a magnetic impurity in a metal yields a criterion for the occurrence of magnetism on the impurity at $T = 0$. If electron-correlation effects are taken into account beyond the Hartree-Fock approximation the conditions for magnetism become severely restricted⁴⁷⁾ and in particular in Anderson's non-degenerate-orbital model the impurity is always nonmagnetic at $T = 0$ ⁴⁸⁾.

On the other hand Nagaoka³¹⁾, using the s-d exchange model, suggested a quasibound-spin state to occur below the Kondo-temperature. According to later authors⁴⁹⁾ the impurity spin might be completely compensated by the conduction electron-spins at $T = 0$.

A connection between Anderson's and the s-d exchange model was made by Schrieffer and Wolff⁴⁹⁾. In the strongly magnetic limit of Anderson's model: $\Gamma_{\pm} \ll |\epsilon_{\pm}|$ they were able to carry out a canonical transformation of Anderson's Hamiltonian into the s-d exchange Hamiltonian. (Γ_{\pm} is the width of the d-state in Anderson's model, $\epsilon_{\pm} = \epsilon_m + U/2 \pm U/2$ where ϵ_m is the energy of the state with magnetic quantum number m and 'spin-up' relative to E_F and U is the Coulomb repulsion between opposite-spin electrons on the d-orbital). The transformation yielded a value for the exchange constant J in terms of parameters from the Anderson model

$$J_m = \frac{-|V_{km}|^2 U}{2S |\epsilon_m| (\epsilon_m + U)} \quad (1.9)$$

for each state the magnetic quantum number m of which being singly occupied. V_{km} is a matrix-element which accounts for the mixing between conduction-band and d-orbital wave functions. S is the spin of the local moment. In principle (1.9) had already been proposed by Anderson and Clogston⁵⁰⁾. The value of J_m is seen to be negative, which leads to a resistance minimum. If the d-orbitals are degenerate we may write

* Anderson⁴⁴⁾ also claims the suggestion that the peculiar susceptibility behaviour of Ir-Fe⁴⁵⁾ might be due to a high T_K . Again, unfortunately, his light was hidden under a bushel.

$$J_m = J = \frac{-V^2 U}{2S |\epsilon_d| (\epsilon_d + U)} = \frac{-2V^2}{SU} \quad (I. 10)$$

where V^2 is an average of $|V_{km}|^2$ and $\epsilon_d = -\frac{1}{2}U$ in the symmetric i.e. most favourable case for magnetism in the Anderson model. The width of the d-states is related to the mixing matrix-elements by

$$\Gamma_{\pm} = \pi \rho_{\pm} (\epsilon_{\pm}) |V_{km}|^2 \approx \pi \rho_{\pm} (E_F) V^2 \quad (I. 11)$$

where ρ_{\pm} is the conduction-band density of states. Thus $J \rho_{\pm} \approx -\frac{2\Gamma}{\pi S U} \approx \frac{-1}{\pi S} \frac{\Gamma}{\epsilon_d}$. It follows that the criterion for the validity of the Schrieffer-Wolff

transformation is equivalent to that for the validity of Kondo's treatment of the s-d exchange scattering problem. In the latter case there is however an additional condition: $T/T_K \gg 1$ which, in view of the logarithmic nature of the Kondo effect might be written $\ln(T/T_K) \gg 1$ i.e. $|J| \rho_{\pm} \ln(E_F/k_B T) \ll 1$, which looks a little more stringent than $|J| \rho_{\pm} \ll 1$.

With the help of (I. 10) one may acquire some qualitative insight into the relation of $T_K \approx (E_F/k_B) \exp(-1/|J| \rho_{\pm})$ to the magnetic situation of the impurity atom (see fig. 1.4).

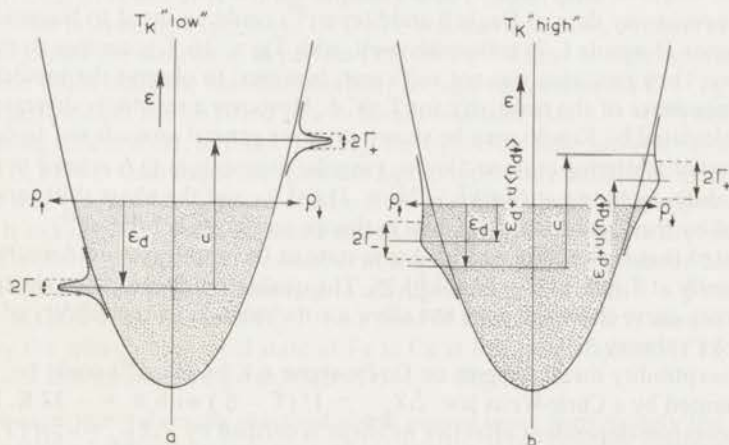


fig. 1.4 Qualitative illustration of the relation between T_K and the parameters of Anderson's model for one d-orbital. ρ_{\uparrow} and ρ_{\downarrow} are the densities of states for two spin-directions. Energies are counted relative to the Fermi-energy E_F ($\epsilon_F = 0$), $\langle n_d \rangle$ is an average occupation number.

a. $\Gamma/U \approx \Gamma/|\epsilon_d| \ll 1$. The lower level is fully occupied: $\langle n_{d\uparrow} \rangle = 1$, the upper level is empty: $\langle n_{d\downarrow} \rangle = 0$. The unperturbed level ϵ_d is broadened but not shifted. The Schrieffer-Wolff transformation is valid. T_K is 'low'.

b. Γ is large. $\langle n_{d\uparrow} \rangle < 1$, $\langle n_{d\downarrow} \rangle > 0$. The unperturbed level ϵ_d is broadened and shifted. The Schrieffer-Wolff transformation is only approximately valid. T_K is 'high'. If not taken too literally one may imagine that a. describes Cu-Mn and b. Cu-Fe. In the case of Al-Mn the spin-up and spin-down 'hump' are both centered at the Fermi-energy, and there is no net magnetic moment.

If the impurity has a well-developed moment in the sense of Anderson's model T_K will be 'low'. If $|\epsilon_d|$ or $\epsilon_d + U$ become smaller T_K will be higher if the conditions for magnetism are less well satisfied. A high spin-value favours a low T_K -value. Although the Schrieffer-Wolff transformation is not valid in the non-magnetic limit, one may extrapolate the ideas qualitatively by conjecturing that 'probably some of the impurities which at conventional temperatures are observed to have zero magnetic moment, are actually the end product of a very high-temperature condensation due to the Kondo effect'⁴³).

The ideas expressed above were employed by Daybell and Steyert¹²) for a reexamination of existing experimental data. By comparing resistivity, thermopower, susceptibility and specific heat of first row transition metals (and Mössbauer effect in the particular case of iron) in several nontransitional hosts they were able to estimate roughly the values of T_K and to account qualitatively for the variation of T_K with position in the transition series of the periodic system.

1.6. A look at some early experiments

We shall discuss the Cu-Fe system extensively in chapters II and III. Here we will only briefly outline the experimental results which showed Cu-Fe to be a dilute magnetic alloy with a Kondo temperature of about 20 K.

The resistivity data of Daybell and Steyert³⁷) could be fitted to Nagaoka's expression (formula I. 7) reasonably well, with $T_K = 16$ K according to the authors. Their precision was not sufficient, however, to observe the predicted T^2 -dependence of the resistivity for $T \ll \Delta$. Moreover a resistivity-divergence like calculated by Kondo may be shown on quite general grounds not to occur. The partial scattering cross-section σ_ℓ (angular momentum ℓ) is related to the phase shifts δ_ℓ by $\sigma_\ell = (4\pi/k_F^2) (2\ell + 1) \sin^2 \delta_\ell$ and the phase shifts are limited by the Friedel sum-rule. For exchange scattering Schrieffer⁴³) suggested that each singly-occupied spin-state at the impurity would scatter resonantly at $T = 0$, so $\sigma = (4\pi/k_F^2) 2S$. The qualitative shape of the electrical resistivity-curve therefore does not allow a conclusion as to the validity of Nagaoka's theory*.

Susceptibility measurements on Cu-Fe above 6 K by Hurd²⁶) could be represented by a Curie-Weiss law: $\Delta\chi_{Fe} \sim 1/(T - \theta)$ with $\theta = -32$ K. If a temperature-dependent effective moment is defined by $\Delta\chi_{Fe} = \mu_{eff}^2(T)/3k_B T$ (per Fe-impurity) and the Curie-Weiss behaviour would be observed down to $T = 0$, μ_{eff} would be zero at $T = 0$. In order to fit their susceptibility measurements Daybell and Steyert used two values of θ : -14 K and -0.045 K, so $\Delta\chi_{Fe} = A/(T + 14) + B/(T + 0.045)$ for $T \gtrsim 50$ mK. This is a rather complicated behaviour, which will be discussed, together with later results by the same authors⁵¹) in chapter II. For the moment it is important only that the value of A corresponds to 3.6 Bohr magnetons per Fe-atom, and B to 0.92 Bohr magnetons. Thus the susceptibility of the Fe-atoms is appreciably smaller than

* The resistivity-curve nevertheless contains a fair amount of information as we will show in the following chapters.

the susceptibility of a free moment down to very low temperatures and the effective moment μ_{eff} as defined above tends to zero. This is an agreement with the idea of a compensated spin.

The most convincing demonstration of the Fe-moment tending to zero with temperature was given by Jensen et al.⁵²). A magnetic moment in a metal produces a spin-polarization of the conduction-electrons, which oscillates in space, and which at large distance from the impurity is proportional to $\cos(2k_{\text{F}}r)/(k_{\text{F}})^3$. These Ruderman-Kittel-Kasuya-Yosida (R.K.K.Y.) spin-density oscillations cause effective magnetic fields to occur at the nuclei around the impurity. If magnetic impurities are randomly distributed in the host the linewidth of the nuclear magnetic resonance-signal at the host-nuclei will be larger than in the pure metal. In the case of short-range magnetic order one would then observe a magnetic field-independent linewidth. In the case of Cu-Fe Jensen et al.⁵²) found a width of the Cu⁶³ resonance-line which was independent of temperature from 0.02 to 0.5 K, proportional to the external magnetic field, and an order of magnitude smaller than what might be expected from higher temperature-data (if the effective magnetic moment would stay the same). The linewidth extrapolated nearly to the value for pure copper at $H = 0$. Apparently the amplitude of the R.K.K.Y.-oscillations is proportional to the total magnetization of the Fe-atom and the conduction-electron-spins coupled to it. At $T \ll T_{\text{K}}$ a magnetic field creates a magnetization at the Fe-site proportional to H and at $H = 0$ the impurity is in a singlet state.

Another interesting experiment on Cu-Fe was carried out by Frankel et al.⁵³) who measured the saturation hyperfine-field on Fe⁵⁷ nuclei in high external magnetic fields using the Mössbauer-effect. At high temperatures ($T \gg T_{\text{K}}$) the hyperfine-field can be fitted to a Brillouin-function with $S = \frac{3}{2}$ ²⁶) but with decreasing temperature, in fixed field H_0 , the hyperfine field saturates at a value H_{sat} (H_0) lower than expected from the high-temperature Brillouin-fit. This means that the magnetization of the Fe-atom is smaller than the free-spin value. If H_0 is increased H_{sat} also increases and extrapolating their results beyond 136 kOe (their highest field) Frankel et al. concluded that above about 235 kOe the Fe-spins would behave according to a Brillouin-function with $S = \frac{3}{2}$ and $H_{\text{sat}} = 80$ kOe at all values of H_0/T . So a field of about 235 kOe is needed to destroy the spin-compensated state of Fe in Cu at low temperatures. If $T_{\text{K}} \approx 20$ K and $g = 2$ this means that $g\mu_{\text{B}}\sqrt{S(S+1)} H_0 \approx 3k_{\text{B}}T_{\text{K}}$.

The experimental results sketched above proved quite convincingly the existence of a low-temperature state of conduction-electron-spins coupled to the local Fe-moment to form a singlet. A number of interesting questions regarding the ground-state remains to be discussed in the following chapters i.e. the question of the long-range negative spin-polarization predicted by Nagaoka³¹), the thermal excitations from the ground-state (specific heat) and the way in which transport properties and susceptibility approach their value at $T = 0$.

Almost simultaneously with the papers on Cu-Fe a paper by Kume was published, proposing another alloy with a high T_{K} -value: Au-V⁵⁴). The peculiar behaviour of Au-V was known already for a long time. Linde⁵⁵) observed a resistance-minimum in Au-V alloys above room-temperature at concentrations above 2 at. % V. From susceptibility measurements above room-temperature, fitted to a Curie-Weiss relation, Vogt and Gerstenberg⁵⁶) found a Curie-Weiss temperature $\theta \approx -100$ to -200 K. Kume⁵⁷) obtained

$\theta \approx -300$ K, measuring from 1000 K down liquid-Helium temperatures. If the impurity-susceptibility is again expressed in terms of a temperature-dependent effective moment $\mu_{\text{eff}}^2(T) = 3k_B T \Delta \chi_V \sim T/(T - \theta)$ it follows that already at room-temperature $\mu_{\text{eff}}(T)$ is smaller than the free-spin value. Apparently in the case of Au-V the formation of the quasi-bound state starts already above room-temperature. If we recall that for Cu-Fe the Curie-Weiss $|\theta|$ obtained from high temperature susceptibility measurements was approximately equal to the estimated Kondo-temperature, we may estimate $T_K \approx 300$ K for Au-V. This value was proposed by Kume. According to Kume⁵⁷⁾ at very low temperatures, the resistivity data of dilute Au-V alloys can be described by $\rho = \rho_0 - AT^2$, which would be in agreement with Nagaoka's theory. Careful measurements show however, that there is no clear T^2 -dependence of ρ in dilute Au-V. In fact the behaviour of Au-V is very complicated as regards the temperature dependence of physical quantities for $T \ll T_K$. We shall discuss this in chapter II.

I.7. Cu-Fe and Au-Fe.

In this section we want to illustrate some of the discussions of the preceding sections with a comparison of Cu-Fe and Au-Fe. In fig. I.5 we show the resistivity of 50 ppm Fe in Cu and in Au in the liquid-helium temperature-region. The Fe-concentration is small enough for Fe-Fe interactions to be unimportant.

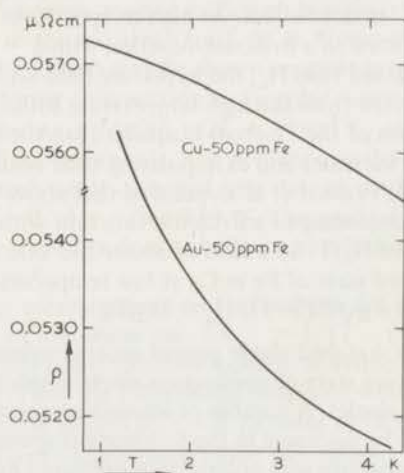


fig. I.5 Comparison of characteristic parts from the electrical resistivity-curves of Cu-Fe and Au-Fe.

The curve of Cu-Fe ($T_K \approx 20$ K) is characteristic for $T < T_K$, the Au-Fe curve is approximately linear in $\log T$, so $T > T_K$ ($T_K \approx 0.3$ K). There is no a priori reason why T_K of Fe in Cu should be higher than T_K of Fe in Au. The electronic density of states (obtained from specific heat) at the Fermi-

energy is in gold 8% higher than in copper. Using the expression $T_K \approx (E_F/k_B) \exp(-1/|J|\rho_1)$ we see that $|J|$ of Au-Fe has to be smaller than $|J|$ of Cu-Fe. It may be that somehow the lowering of E_F reduces the mixing-parameter V_{kd} (section I.5), thus narrowing the virtual level. One might argue then that formula (I.9) would lead to a lower $|J|$ and thus a lower T_K . It should be remarked, by the way, that all first-row transition-atoms in copper have a higher T_K than in gold. Anyhow, already a small change of $|J|\rho_1$ is sufficient to cause a large sweep of T_K .

When the Fe-concentration in copper is increased the shape of the curve in fig. I.5 stays qualitatively the same. In Au-Fe a maximum of the resistance develops in the liquid-helium temperature-region, at about 0.1 at.% Fe and T_{max} increases with Fe-concentration. This difference in behaviour may now be easily understood. As remarked in the preceding section, the amplitude of the R.K.K.Y. spindensity-oscillations is strongly suppressed below T_K by the formation of the spin-compensated state about the Fe-atoms. So the Fe-Fe interactions, necessary to reduce the "Kondo-scattering" are almost absent for Cu-Fe (not Au-Fe) at liquid-helium temperatures. An external magnetic field is neither effective, because the effective moment is reduced.

One may define an ordering-temperature T_O for uncompensated spins by equating $k_B T_O$ to the interaction energy²⁵ $c (J^2/E_F) S(S+1)$. If $J \approx 0.5$ eV and $S = \frac{3}{2}$ we have $T_O \approx 20$ K/at.%. This is roughly the temperature at which a resistivity-maximum is observed in Au-Fe. In order to observe such interaction effects in Cu-Fe the Fe-concentration has to be so large that the interaction energy is appreciable already above the temperature-region where spincompensation effects become important. Thus T_O should be higher than T_K , which means that $c > 1$ at.% for Cu-Fe. Indeed at such concentrations resistivity-maxima have been observed by Svensson⁵⁹ on severely cold-worked alloys and by Korn⁶⁰ on Cu-Fe films, evaporated on a substrate kept at 77 K. The fact that only under such special circumstances a resistance-maximum is observed has certainly to do with the poor solubility of Fe in Cu.

Other types of interaction may change the shape of the resistivity curve already at lower concentrations. The spin-compensated state has a certain extension in space. As soon as ranges of spin-correlations coupled to different impurities tend to overlap each other, the impurity will start to develop a moment again at $T < T_K$. One may also put it differently: the conditions for two impurities, near to each other, to be magnetic in the sense of Anderson's model may be satisfied, while these impurities are non-magnetic when isolated⁶¹). These concentration effects in a range where magnetic ordering is still unimportant are quite interesting and we will pay attention to them in chapters II and IV.

When dissolving Fe in Cu-Au alloys one expects to see the Kondo-temperature shift continuously, when the host composition is varied from Cu to Au. In the s-d exchange model the shape of the resistivity-curve depends only upon the spin S of the impurity, its Kondo-temperature, and the band-structure of the host⁶²). If potential-scattering at Fe is supposed not to change appreciably between Cu and Au one may observe different parts of the 'universal' iron-resistivity curve for different Cu-Au-hosts and match them together to obtain the whole curve. This is important since theory predicts that the resistivity may keep changing along several decades in temperature³⁰) (see also section I.8)

whereas experimentally, above 10 K it is difficult to obtain the impurity-resistivity due to deviations from Matthiessen's rule, and below 0.1 K precise resistivity measurements are difficult to perform.

One can also study the behaviour of magnetic ordering in the resistivity (resistivity-maximum) when the Fe-concentration is chosen such that T_K moves from above T_O (Cu-Fe) to below T_O (Au-Fe) when going through the Cu-Au series. We have done this⁶³, measuring the resistivity of 0.15 at. % Fe in seven different hosts (fig. I.7). Going towards copper from the gold-rich end we see the temperature of the resistivity-maximum decreasing and $\rho_{\max} - \rho_{\min}$ increasing. Two effects are responsible. Firstly the shift of T_K ,

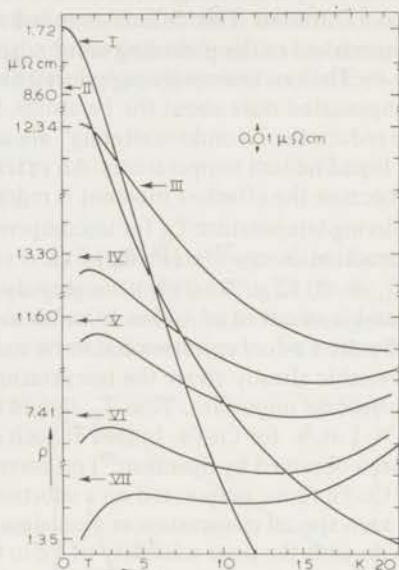


fig. I.6 Magnetic ordering versus spin-compensation in the electrical resistivity of Cu-Au alloys containing 0.15 at. % Fe. I: Cu, II: Cu_5-Au_1 , III: Cu_4-Au_2 , IV: Cu_3-Au_3 , V: Cu_2-Au_4 , VI: Cu_1-Au_5 , VII: Au.

which is modest near Au, and quite large at the copper-rich end of the series^{64,65}). Secondly the large electron-scattering by the host-alloy which reduces the R.K.K.Y.-interaction between Fe-moments^{40,41}). Beyond Cu_3-Au_3 the residual resistivity decreases again, but $\rho_{\min} - \rho_{\max}$ continues to increase. In this region T_K if of the same order of magnitude as T_O and spin-compensation takes over in further reducing the Fe-Fe interactions. The temperature of the resistance-maximum continues to decrease although it cannot be observed for hosts II and III) and in Cu-Fe the maximum is at $T = 0$. This is not a maximum due to magnetic ordering anymore, although a spin-compensated state is in principle a magnetically ordered state, but on an atomic scale only.

We have also studied the resistivity of Cu-Au alloys with a quite low Fe-concentration, such that Fe-Fe interactions are small⁶⁴). In that case one should be able to construct the supposedly universal curve for Kondo scattering at Fe.

We shall not repeat the discussion of ref. [64], but make only a few remarks, in particular in connection with the extensive research of Loram et al.⁶⁵⁾ on low concentration (Cu-Au)-Fe alloys, which was published recently. These authors have indeed been able to match their results on various Cu-Au hosts together. In spite of the careful experiments of Loram et al. we believe that there are some problems with (Cu-Au)-Fe. Firstly, T_K (but also J) appears to decrease rather rapidly with increasing Au-concentration at the Cu-rich side. There is no a-priori reason why J should vary linearly with host-composition. It is quite possible however that Cu-Au is not a homogeneous host-alloy to Fe, but that Fe prefers a gold-rich environment since the solubility of Fe in Au is much higher than in Cu. Even Jaccarino-Walker type¹⁰³⁾ of local-environment effects may be of importance. In that case one cannot be sure that the different parts of a universal resistivity-curve will show up in (Cu-Au)-dilute Fe alloys. In this connection we want to make a second remark. At the Au-rich side of the Cu-Au alloy series containing 0.02 at. % Fe we observed resistivity curves linear on a log-T scale in a temperature range (1 - 20 K) of more than one decade apparently above T_K ⁶⁴⁾. We therefore suggest that either the universal curve might cover a wider temperature-region than proposed by Loram et al.⁶⁵⁾ or that this is only the case for Fe in some Cu-Au hosts, in which case a universal curve for scattering by Fe might not exist at all.

One may think of various other binary alloy-systems of interest to be studied as a host to transition metal impurities. The work of Sarachik et al. on Fe in Nb-Mo and Mo-Re alloys¹⁸⁾ and of Caplin on Fe in ϵ -phase Cu-Zn alloys⁶⁶⁾ are nice examples. We have also considered other possibilities like Fe and Co in Au-Pd alloys, V in Pd-Au and Au-Cu alloys. Au-Fe shows the Kondo-effect as discussed before, dilute Pd-Fe alloys are ferromagnetic. Dilute Pd-Co alloys are also ferromagnetic, whereas Co in Au has a Kondo-temperature of about 300 K¹⁶⁰⁾. We have performed several trial experiments, but did not continue our work on ternary alloys for two main reasons. The first reason is a metallurgical one. In most cases the magnetic impurity to be considered has a different solubility in each of the components of the host, which may complicate the interpretation of the results. We mentioned this difficulty above with regard to (Cu-Au)-Fe. The second reason is that theoretical developments at the time of our experiments on (Cu-Au)-Fe suggested that it might be interesting to pay attention to the low-temperature limit ($T \ll T_K$) of some physical properties in dilute alloys exhibiting the Kondo-effect.

1.8 Some theoretical expressions for $T \ll T_K$

Nagaoka's treatment of the Kondo-effect was reconsidered by Hamann⁶²⁾. He started with the equations of motion, as decoupled in lowest non-trivial order by Nagaoka³¹⁾, but found a better — although approximate — solution, which was not artificially divided up into a high-temperature ($T > T_K$) and a low-temperature ($T < T_K$) part. No instability was observed at $T \approx T_K$ ³¹⁾. Instead, the resistivity varied smoothly with temperature, attaining the unitarity-limit at $T = 0$, and T_K determined only the scale of the temperature variation. In Hamann's theory there was apparently no place for a (quasi-) bound state below T_K . Of course this did not lead to a rejection of Cu-Fe as a

dilute alloy with a $T_K \approx 20$ K since too many experiments supported this idea by now. Hamann's result for the resistivity reads (see fig. 1. 7):

$$\rho_{\text{res}} = \frac{hc}{ne^2 k_F} (1 - \ln(T/T_K) (\ln^2(T/T_K) + S(S+1)\pi^2)^{-\frac{1}{2}}) \quad (I. 12)$$

This curve has an inflection point at $T = T_K$, where ρ is linear on a logarithmic temperature-scale, and

$$\frac{d\rho}{d \ln T} = \frac{2c}{ne^2 k_F} \frac{h/2\pi}{\sqrt{S(S+1)}} \quad (I. 13)$$

One may also expand (I. 12) for $\ln T \gg \ln T_K$, i.e. $|J| \rho_1 \ln(D/k_B T) \ll 1$ and then obtains (D is the bandwidth):

$$\rho_{\text{res}} = \frac{hc}{ne^2 k_F} \frac{\pi^2 S(S+1)}{2} (J\rho_1)^2 [1 + 2J\rho_1 \ln(T/D)] \quad (I. 14)$$

This is equal to Kondo's result (I. 4) *. From (I. 13) and (I. 14) it follows that $d\rho/d \ln T$ of Hamann's expression (I. 13) has to be multiplied by $(J\rho_1)^3 (\pi^2 S(S+1))^{3/2}$ in order to obtain $d\rho/d \ln T$ of Kondo's expression. This factor may be quite small and one has to be aware of the difference.

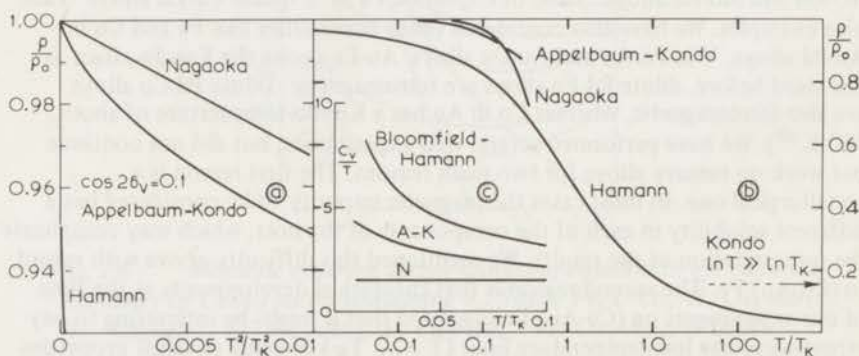


fig. 1.7 Impurity contribution to the electrical resistivity and the specific heat according to various theoretical predictions for $Spin = \frac{1}{2}$

- Normalized resistivity versus $(T/T_K)^2$. $d\rho/d(T^2)$ diverges at $T = 0$ for both Hamann's and Appelbaum-Kondo's expressions.
- Normalized resistivity versus $\log(T/T_K)$. According to Hamann the 'transition' occurs along several decades in temperature. This temperature region is even broader for $S > \frac{1}{2}$. (see also ref. 30). At the bottom right it has been indicated that Kondo's original result is applicable far above T_K only.
- Specific heat divided by temperature on an arbitrary vertical scale versus T/T_K .

* Kondo's J is by definition a factor of 2 smaller than Nagaoka's and Hamann's J . We will further use Nagaoka's definition.

In fact Kondo's term is only one out of a series²⁸⁾ and is not necessarily the dominating term if not $\ln T \gg \ln T_K$.

The integral equation derived by Hamann and solved approximately by him⁶²⁾ was solved exactly by Bloomfield and Hamann⁶⁸⁾. The impurity specific heat was computed for $S = \frac{1}{2}$ and its temperature-dependence could be well described by $C_V \sim T^{0.57}$ from $T/T_K = 10^{-4}$ up to nearly $T/T_K = 10^{-1}$. According to Zittartz and Müller-Hartmann⁷⁰⁾, for $T \ll T_K$ and $\ln(T/T_K) \gg 1$: $C_V \sim \ln^{-4}(T/T_K)$. The electrical resistivity was not computed with the exact solution. This was done later by Fischer⁶⁹⁾ who included potential scattering and obtained approximate expressions for the transport properties for the case of large normal scattering compared to exchange scattering. As to the resistivity, Hamann's approximate solution (I. 12) and the exact solution are identical if $|\ln(T/T_K)| \gg 1$.

Appelbaum and Kondo¹⁰⁵⁾ calculated the electrical resistivity and the specific heat using a model for a singlet ground state of a magnetic impurity in a metal proposed by Kondo. For the resistivity their result may be written to a good approximation:

$$\rho = \rho_0 \left[\cos^2 \delta_V - \frac{16}{3} \cos 2\delta_V \left(\frac{T}{T_K} \ln(T/T_K) \right)^2 \right] \quad (\text{I. 15})$$

where δ_V is the phase shift due to potential scattering (see fig. I. 7). For the impurity specific-heat Appelbaum and Kondo obtained:

$$C_V \sim T \ln(T/T_K) \quad (\text{I. 16})$$

The A.K.-theory is a ground-state theory, so (I-15) and (I. 16) should be valid only for $T < T_K$.

Another singlet ground-state model was proposed by Anderson⁷¹⁾. From a preliminary calculation of the excitation-spectrum he predicted an excess density of state varying as $(E - E_F)^{-1/2}$. On this basis one might expect the susceptibility to be proportional to $T^{-1/2}$ and the specific heat proportional to $T^{+1/2}$. This last temperature dependence should be compared with Bloomfield and Hamann's $T^{+0.57}$.

The peculiar temperature dependences quoted above have played an important role in analyses of experimental results. Except for Anderson's work⁷¹⁾ they are based on theories using the s-d exchange model. Objections have been raised against calculations of singlet ground-state properties using a model which assumes the existence of a constant J . Suhl⁷²⁾ has argued that if J would arise from Coulomb interaction together with the exclusion-principle and if there is no spin-flip scattering at $T = 0$ (in a singlet-state) then J should be zero. So it is not correct to keep J constant. Instead, J should be calculated self-consistently. According to Heeger¹³⁾ even for a singlet-state there would be spin-flip scattering near to the impurity and the spin-flip amplitude would be zero only at large distances. Thus there would be no discrepancy between the idea of a singlet-state and the assumption of a constant J . However that may be, an additional question is to which extent the s-d exchange model may describe a real dilute magnetic alloy. In view of the difficulties encountered in solving the s-d model (in which the existence of a magnetic moment is assumed) for

$T \ll T_K$ it appeared worthwhile to approach the problem from the non-magnetic side. That is to say investigating a model for a nearly magnetic impurity and the relation of its parameters to the possible occurrence of a temperature-dependent susceptibility and/or resistivity. This approach was made in the spin-fluctuation theories. Spin-fluctuations were first introduced into the dilute-alloy problem by Lederer and Mills (see ref. 73 and references contained therein) to explain the properties of Pd-Ni alloys. For the case of a very weak resistance-minimum which they had observed in Al-Mn and Al-Cr, Caplin and Rizzuto⁷⁴) proposed spin-fluctuations to explain qualitatively the temperature-dependence of ρ (containing a small T^2 -term) and the temperature-independence of the enhanced susceptibility. This type of spin-fluctuations was considered theoretically by Rivier and Zuckermann⁷⁵). A spin-fluctuation theory was at the same time also developed by Suhl and coworkers⁷⁶). As far as predictions on physical quantities have come out one can say that the general physical picture is a locally enhanced density of states at the site of an impurity which is near to being magnetic. Consequently, the impurity specific-heat should be proportional to T and the susceptibility at low temperatures should be enhanced Pauli-like. The resistivity approaches as T^2 its value at $T = 0$. Some difficulties should however be mentioned. Recently Hamann⁷⁷) studied the Anderson-model in the 'renormalized random-phase approximation' which Suhl et al.⁷⁶) had applied to the Wolff-model. He obtained a susceptibility which is constant at low temperatures and Curie-like at high temperatures. The Curie-constant however, obtained from a low-temperature Curie-Weiss fit was much too small. The resistivity contains a T^2 -term at low temperatures and a $\log T$ -term at high temperatures. The characteristic spin-fluctuation temperature (or Kondo temperature) however, which appears in the expression for the resistivity is orders of magnitude smaller than T_K obtained with the same parameters from Anderson's model using the Schrieffer-Wolff transformation. This signals some shortcomings of the R.R.P.A.-treatment and shows that we should not take the predicted temperature-dependencies too seriously.

We should recall here Nagaoka's result for the resistivity (I. 7) and also mention his calculations of the impurity specific-heat which gives

$$C_v = \frac{2\pi}{3} \frac{T}{\Delta} \quad (I.17)$$

Notwithstanding the work of Hamann⁶²) and Bloomfield and Hamann⁶⁸) we quote Nagaoka's expressions in view of future comparisons with experimental results. For the same reason we also mention Klein's work⁷⁸). Klein used Takano and Ogawa's model, which is analogous to Gorkov's treatment of superconductivity, just like Nagaoka borrowed the method used by Zubarev. Klein obtained expressions for the resistivity and the specific heat similar to Nagaoka's. In addition he derived an expression for the low-temperature susceptibility per impurity per unit volume:

$$\chi = \frac{5.4}{\pi} \frac{\mu_B^2}{k_B T_K} \left[1 - 2.4 \left(\frac{T}{T_K} \right)^2 \right] \quad T \ll T_K \quad (I.18)$$

We remark that, as far as theories predict simple power-laws for the temperature-

dependencies of physical properties, these are of the same form as for an electron-gas, the band-width or Fermi-energy being replaced by $k_B T_K$.

At this stage we do not want to give an opinion as to the applicability of the expressions which we quoted. We have only shown that in 1968 a wealth of theoretical predictions was available to the experimentalists and that interest in the ground-state problem made measurements of physical properties at $T \ll T_K$ quite worthwhile.

1.9. Suitable systems

In order to investigate the properties of the quasibound state, and in particular its ground-state properties, one would like to have the disposal of various alloys with a T_K in the liquid-helium temperature-region or higher and with favourable metallurgical properties. Soon after the publication of the papers mentioned in section I. 6 several systems with a suitable T_K -value were found. As regards dilute alloys of transition-metals in non-transitional hosts, this followed readily from the considerations of Schrieffer⁴³) as applied to existing experimental data by Daybell and Steyert¹²). Cu-Co and Au-Co have a Kondo-temperature above room-temperature. This is very favourable for the study of the limiting low-temperature ($T \ll T_K$) behaviour of resistivity and specific-heat. Both alloys have a serious disadvantage however, in that Co-atoms show a tendency to form clusters, which hampers the observation of effects due to non-interacting impurities.

Cu-Cr has a T_K of about 2 K^{13,58}). This alloy is therefore favourable for observation of physical properties around the 'transition-temperature' T_K . T_K is probably too low for a careful study of the ground-state properties, in particular concerning specific-heat, resistivity and susceptibility. One can however observe the destruction of the quasi-bound state by easily attainable external magnetic fields (of order 30 kOe). Upon decreasing the temperature Daybell and Steyert⁵⁸) observed in Cu-Cr a lower saturation-value of the resistivity with increasing magnetic field and saturation started at correspondingly higher temperatures. Recently Triplett and Phillips⁷⁹) observed an increasingly 'free-spin'-like behaviour of Cr by measurements of the specific heat of dilute Cu-Cr alloys in magnetic fields up to 38 kOe.

Zn-Mn and Zn-Cr have a T_K of about the same magnitude as Cu-Cr. Al-Cr and Al-Mn might be considered to have a high Kondo-temperature, i.e. a spin compensated at all temperatures below room-temperature. Currently however the behaviour of these alloys is interpreted in a different way, namely as non-magnetic alloys showing localized spin-fluctuations. (see the remarks in section I. 8).

Resistance minima have also been observed in dilute alloys of first row transition metals in other transition metals, and in some cases with a high T_K . Co in Mo is much an example, with a T_K of the same order of magnitude⁸⁰) as Cu-Fe. Mo-Co would be as ideal as Cu-Fe, but the high melting-temperature of Mo, its hardness and the difficulty to obtain it sufficiently pure are serious drawbacks for studying the magnetic state of Co in Mo below T_K . (For N.M.R. there are no problems). A value of T_K also comparable to Cu-Fe has been found for Ce in Y by Sugawara⁸¹). This alloy should be ideal for studying the

impurity specific-heat below T_K , if sufficiently pure Y can be obtained. Precise study of the resistivity is difficult however because for a high precision one needs a large shape-factor (see chapter II) and Y is rather brittle which hampers wire-drawing. Besides, with rare-earth metals one has to consider the possibility of crystal-field splittings which may cause phenomena analogous to or interfering with the Kondo-effect. In the case of Ce however it is not unlikely that the orbital momentum is quenched, like in transition metals, since the 4f-orbital is not as localised as in other rare-earths.

We have not yet mentioned many systems in addition to Cu-Fe and Au-V which should be practically suitable for studies at $T \ll T_K$. In fact, in 1968, we found only one, and today there are not many more. The alloy which we first investigated was Pd-Cr. Schwaller and Wucher⁸²⁾ had measured the resistivity of some alloys up to 4 at. % Cr and found minima at temperatures up to 50 K, without a tendency toward a resistance-maximum at lower temperatures. This was a hopeful sign of a high Kondo-temperature. After some preliminary measurements showing the low-temperature saturation behaviour characteristic of the Kondo-effect⁸³⁾ we found a T^2 -dependence at low temperatures and low impurity-concentrations⁸⁴⁾. We estimated the Kondo-temperature to be of order 200 K⁸³⁾.

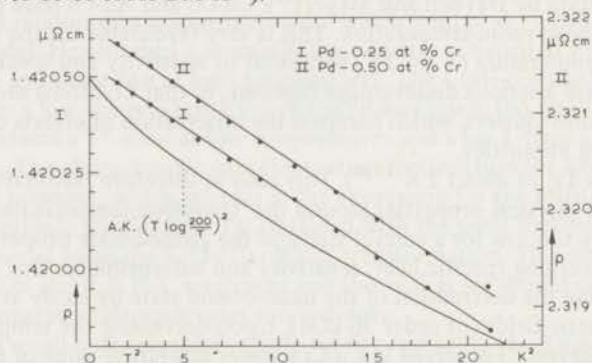


fig. 1.8 Resistivity of two Pd-Cr alloys versus T^2 . Indicated concentrations are nominal values. For convenience of plotting the pure-Pd resistivity was not subtracted. The pure-Pd T^2 -term is $+2.7 \times 10^{-5} T^2 \mu\Omega \text{ cm}$.

Undoubtedly a T^2 -term is most appropriate to describe the Pd-Cr resistivity at small Cr-concentration. Application of Hamann's expression (I. 12) is certainly out of the question and so is Appelbaum-Kondo's. In the latter case one has to be careful however. In order to make a clear distinction between A-K. and T^2 the resistivity-measurements have to be performed with particular precision. This is quite possible experimentally. As to the impurity specific-heat a similar distinction is much more difficult to make.

The T^2 -dependence of Pd-Cr could be observed in a very convenient temperature region: liquid helium. Having obtained this result (and the specific-heat, to be described in chapter IV) we found it a challenge to tackle Cu-Fe. If we guess *, that ground-state properties may be observed if $T < 0.1 T_K$

* This is indeed a guess. If Hamann's theory were applicable⁶²⁾, one should have $\ln(T_K/T) \gg 1$ which is a much more severe condition.

then in the case of Cu-Fe we should perform measurements in a not too narrow temperature region below 2 K, down to 0.1 K for example, and with a fair precision. We have succeeded in doing so and show a preliminary result⁸⁵⁾ in fig. 1. 9. We may repeat a remark made above for Pd-Cr, that careful

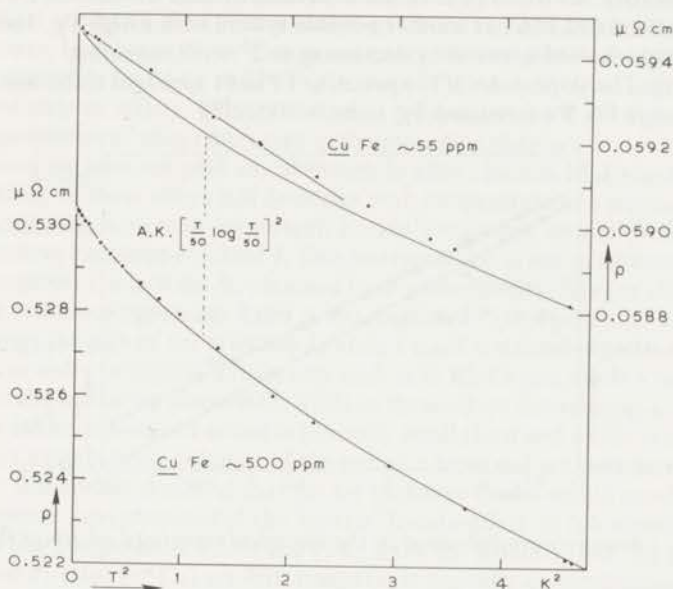


fig. 1.9 Electrical resistivity of two Cu-Fe alloys vs. T^2 , compared with the Appelbaum-Kondo expression. The value $T_K = 50$ K is obtained from the fit to the 500 ppm alloy. Indicated concentrations are estimates.

measurements were clearly necessary to allow an unambiguous distinction between the Appelbaum-Kondo expression and T^2 . The possibility of fitting to the A.K.-expression (I. 15) depends of course on the temperature-region considered. Thus Loram et al.⁶⁵⁾ were able to fit their Cu-Fe results from about 1 – 14 K, but not at the lowest temperatures. As the A.K.-theory is essentially a ground-state theory this means a disagreement between theory and experiment. For the most concentrated alloy of fig. 1. 9 we were able to construct a fit to the A.K.-expression down to very low temperatures, with a reasonable value of T_K , in view of estimates made by other authors. This fit is not possible for the more dilute alloy. Apparently in the 500-ppm alloy Fe-Fe interactions do occur. This is an important point, because Heeger in his review article¹³⁾ devotes ample attention to the Appelbaum-Kondo theory and quotes several resistivity results fitting into this theory. In our opinion the fits are only possible thanks to poor experimental accuracy or too high impurity concentration. So, in addition to the condition of precision, one has a condition of low impurity-concentration. As a rule of thumb one should take $c < T_K/T_F$ (or $T_{s,f}/T_F$ in the case of spin-fluctuations). The origin of this rule will be explained in section II. 6. For Cu-Fe it means $c < 0.02$ at. %. The condition becomes more serious for alloys with a lower T_K and this emphasizes again the need for precise

experiments. In chapter II we will show that the resistivity may be an even more complicated function of concentration than indicated in fig. I. 9. We shall maintain however the T^2 -dependence for sufficiently low temperature and Fe-concentration as suggested by fig. I. 9.

The similarity of Pd and Pt as to the behaviour of their dilute alloys with Ni, Co and Fe suggested Pt-Cr as another possible system with a high T_K . Indeed measurements showed a resistivity decreasing as T^2 with increasing temperature. The slope $-d\rho/d(T^2)$ per at.% Cr in Pt appeared to be somewhat smaller than in Pd. We estimated T_K to be $\approx 300 \text{ K}^{86}$.

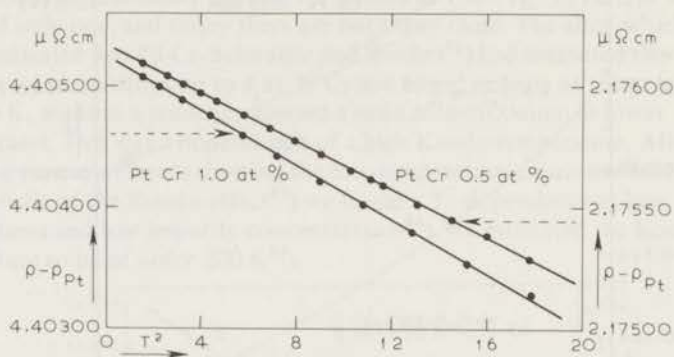


fig. I.10 Impurity-contribution to the electrical resistivity of dilute Pt-Cr alloys.

In fig. I.10 a difference in slope between the two lines may be observed while the two resistivity-scales differ by a factor of 2 and the two residual resistivities by nearly a factor of 2. This difference in slope is a real effect. It occurs also in Pd-Cr and Cu-Fe. We think the effect is a general feature of alloys exhibiting Kondo-scattering. It has probably the same origin as the critical concentration T_K/T_F introduced above. We will discuss this problem in chapters II and IV.

We have not yet reported on Au-V. In this alloy the situation regarding the temperature-dependence of physical quantities below T_K is slightly more complicated. We shall discuss some resistivity and specific-heat results on Au-V at the end of chapter II, in connection with Cu-Fe.

I.10. Program and present situation

In the preceding sections we have given a brief and rather personally coloured view of the history of the Kondo-effect. This was done mainly to provide the necessary introduction to the subject and to describe how we arrived at our investigations. We have mainly written about the resistivity because the history of the Kondo effect is to a large extent the history of resistivity-measurements and calculations.

Our program is now clear. We have at our disposal four dilute magnetic alloys (Cu-Fe, Au-V, Pd-Cr, Pt-Cr) which can be prepared easily, have a convenient Kondo-temperature and are ductile, so that wire drawing for resistivity-experiments is not difficult. We shall study on these systems the

temperature- and concentration-dependence of some physical properties below T_K . In chapter II we discuss the resistivity of Cu-Fe and the relation of our results to experiments of others on specific-heat, susceptibility and nuclear magnetic resonance. At the end of chapter II we also pay some attention to the resistivity and the specific-heat of Au-V. In chapter III we analyse experimental results on the Lorenz-number of Cu-Fe and discuss also the thermopower. In chapter IV we discuss resistivity, thermopower and specific-heat measurements on Pd-Cr and Pt-Cr. In chapter V we shall try to summarize the present state of affairs. This amounts to a comparison for $T \ll T_K$ of the physical properties of alloys discussed in the preceding chapters.

Until now we have not paid any attention to alloys such as Rh-Fe and Ir-Fe. The resistivity of these alloys still decreases with temperature in a region where phonon scattering is no more important. Kondo¹⁾ suggested an interpretation using a positive exchange-constant J . This interpretation is not in agreement with the negative Curie-Weiss- θ , obtained from susceptibility, like for alloys showing a resistance minimum. Later it was suggested¹⁶⁾ that potential-scattering might change the sign of the effective J , while J itself remained negative. However, in order to explain a resistivity such as in Rh-Fe one needs a rather large potential-scattering phase-shift, while in these alloys the valency-difference between host and solute is generally small (host and solute occur in the same or neighbouring columns of the periodic table and are both transition-metals). It is therefore doubtful that the s-d exchange model would provide the appropriate interpretation of the 'reverse' Kondo-effect. It is interesting to make a few comparisons. Pd-Cr and Pt-Cr show the Kondo-effect. Pd-(Mn, Fe, Co) and Pt-(Mn, Fe, Co) are ferromagnetic at impurity concentrations of about 1 at.%, while Pd-Ni is ferromagnetic above 2 at.% Ni and Pt-Ni above 40 at.% Ni. Pd-Ni and Pt-Ni (both isoelectronic) show an enhanced positive T^2 -term in the resistivity at low temperatures, approximately proportional to Ni-concentration below 2 and 40 at.% Ni respectively. Rhodium is next to palladium in the periodic table. Rh-Cr shows a weak resistance-minimum, in Rh-(Mn, Fe, Co) the impurity-resistivity increases with temperature at low temperatures. (Rh and Co are iso-electronic). Rh-Ni shows no peculiarities in the resistivity⁸⁸⁾. A resistance-minimum is frequently (or always?) associated with a scattering-resonance and at $T = 0$ the resistivity is at its maximum value. If interpreted in terms of spinfluctuations, increasing of T above zero causes the scattering to move away from the resonance and thus the resistivity to decrease⁷³⁾. In systems like Pd-Ni and Rh-Fe the residual resistivity is small. Increase of T from zero causes increase of scattering by an increasing amount of spin-fluctuations excited. Probably one day a spin-fluctuation-theory will be developed providing a unified interpretation of both the Cu-Fe and the Rh-Fe type of resistance-anomaly. However, the Kondo-effect was discovered by using the s-d exchange model and if the s-d model has a meaning in describing real alloys, it will probably be only for alloys showing a resistance-minimum. We shall therefore confine ourselves to such systems, and touch upon the others only briefly, if necessary.

Since we started our exploration of temperature-dependencies below T_K a large amount of theoretical work has been published, and new papers continue to appear. Anderson (unpublished) has abandoned his ground-state theory⁷¹⁾. Hamann and Appelbaum⁸⁹⁾ found important corrections to the calculation of Appelbaum and Kondo and arrived at the conclusion that low-temperature

properties cannot be uniquely predicted on the basis of A.K.'s trial starting wave-function. From the preliminary experimental results shown in the preceding section it is clear that the theory of Hamann⁶²) and Bloomfield and Hamann⁶⁸) does not describe the actual situation. As this theory is an exact solution of Nagaoka's decoupled equations of motion the essential physics for $T \rightarrow 0$ is apparently lost in this decoupling. This is emphasized by the fact that Zittartz finds⁹⁰) a negative susceptibility at $T = 0$ for spin = $\frac{1}{2}$. An exact solution for the s-d exchange Hamiltonian for $J > 0$ and $S = \frac{1}{2}$ has recently been obtained by Anderson et al.⁸¹). For $J < 0$ (the case of a resistance-minimum) these authors did not obtain an exact solution, but were able to draw some important conclusions. Results divergent at $T = 0$ as obtained earlier are now out of the question. Thus for example the impurity-susceptibility is finite at $T = 0$. On the basis of the exact solution of Nagaoka's equation Hamann⁶²) and Zittartz⁹¹) had concluded that no spin-compensated state like proposed by Nagaoka would exist. According to Anderson et al. Nagaoka's original conjecture is actually true: a low-temperature bound singlet-state does indeed exist. We quote: 'all magnetic impurities at some scale behave just like ordinary ones'. The scale is determined by the Kondo-temperature.

If Nagaoka's idea of a bound-state is correct why should not his result for the t-matrix at $T \ll T_K$ also be correct (although the calculation was wrong)? This is in fact what experiments indicate (chapter II, III).

Not only the s-d exchange model, but also models which do not assume the existence of a magnetic moment at the impurity (like the spin-fluctuation-theory of Suhl et al.) continue to be investigated. And just as in the s-d case the problem is far from being settled. In the recent work of Appelbaum and Penn⁹²) for example a t-matrix is computed numerically, which varies rapidly at the Fermi-energy and suggests an electrical-resistivity behaving more like Hamann's expression (I. 12) than like a simple power-law.

Summarizing: theory is still in a state of development and there is an apparent need for precise experimental results at $T \ll T_K$, not many of which have been published so far.

CHAPTER II

THE LOW-TEMPERATURE LIMIT OF THE KONDO-EFFECT IN COPPER-IRON AND GOLD-VANADIUM.

II. 1 Scope and motivation, summary of results.

In this chapter we will mainly be concerned with the Copper-Iron system. We will also discuss Au-V, though not as extensively and only in relation to the results on Cu-Fe.

Cu-Fe was the first dilute alloy proposed³⁷⁾ to have a Kondo-temperature (16 K) in an easily accessible temperature region and to exhibit a 'spin-compensated state' like conjectured by Nagaoka. Since then Cu-Fe has been extensively investigated, and new results continue to become available. This is quite understandable, because Cu-Fe is probably the system on which the greatest variety of experiments can be performed at temperatures $T \lesssim T_K$. Besides, some peculiar effects in low magnetic fields ($H \approx 1000$ Oe), have been observed, the interpretation of which is important to the picture one has about the ground-state of Fe in Cu.

Not only from the experimental, but also from the theoretical point of view Cu-Fe is interesting. Firstly there is a general interest in physical properties at $T \ll T_K$. Secondly the lower T_K , the greater the possibility that the s-d exchange model will apply. An alloy with a high T_K may be non-magnetic because the conditions for magnetism are not satisfied ('Hartree-Fock demagnetization'). An alloy with a low T_K is more likely to be non-magnetic at low temperatures due to spin-compensation. This may occur within the s-d model, which has been and is being investigated widely by theorists. Cu-Fe is therefore interesting because its T_K may be the lowest value for which experimentally reliable conclusions can be obtained as to the temperature-dependence of physical properties near to the ground-state.

There seems to exist a growing belief in simple power-laws among theorists^{73, 140)}. We share that belief, but we think that it does not yet rest upon a vast and reliable amount of theoretical and experimental information. So a careful investigation of the Cu-Fe system should be welcome. The Kondo-effect is due to electron-scattering by non-interacting magnetic impurities. Thus information on ground-state properties should be obtained in a concentration-region where all impurity properties are proportional to the concentration. Deviations from proportionality with concentration may provide additional information regarding the low-temperature state of the impurity.

In this chapter our contribution to the solution of the Cu-Fe problem consists of a number of very precise resistivity measurements on dilute alloys containing from 30 to 1000 ppm Fe. We maintained a precision of 1 part in 50000 down to 50 mK and in external magnetic fields of 0, 1000 and 2000 Oe. Our main results are:

1. Below 1 K ($T \lesssim 0.05 T_K$) the temperature-dependent part of the resistivity caused by non-interacting Fe-atoms in copper is most probably proportional to T^2 .

2. Deviations from this simple temperature-dependence are observed and are probably due to magnetic iron-pairs (not necessarily nearest neighbours) with a T_K of about 0.1 K. The resistivity contribution by the 'pairs' is proportional to $\ln T$ and can nearly be quenched in an external magnetic field of 2000 Oe, below 0.1 K. We were able to quantitatively relate our evaluation of the contribution of pairs to results of other authors on specific heat and susceptibility.
3. The Kondo-temperature, even at Fe-concentrations below 100 ppm, is not constant but seems to decrease with increasing Fe-concentration.
4. We compare our results with the transport relaxation-time of Nagaoka, which leads to expression (1.7) for the resistivity. This may be of interest in view of the fact that according to Anderson et al.⁹¹⁾ Nagaoka's original conjecture of a low-temperature bound-state is actually correct. If suitable modifications for potential-scattering are applied, Nagaoka's low-temperature solution describes the resistivity, thermoelectric power and heat conductivity for $T \ll T_K$ (We anticipate the results of chapter III).
5. We have found indications that also the concentration-dependence may be accounted for by Nagaoka's work. This latter statement however cannot be as definite as the preceding points.

II. 2. Previous experiments on Copper-Iron

II.2.1. Transport properties

We quote only the two most recent papers on the resistivity. Daybell and Steyert measured the electrical resistivity of two dilute Cu-Fe alloys down to 40 mK⁵¹⁾. Their relative precision of 0.3 % does not allow a comparison with theoretical expressions, nor a conclusion as to the presence of a T^2 -term. Our own relative accuracy is a factor of 100 better which is not superfluous.

In their investigation of the (Cu-Au)-Fe system Loram et al.⁶⁵⁾ also measured the electrical resistivity of two Cu-Fe alloys (0.01 and 0.04 at. % Fe) from 0.5 K up to 300 K. According to these authors, a fit to the Appelbaum-Kondo expression (1.15) is possible above about 2 K up to 20 K. The Kondo-temperature determined in this way decreases with increasing Fe-concentration. The significance of such A.K.-fits is limited however, because the A.K.-theory is a ground-state theory so that one should compare experimental results with theory for $T \rightarrow 0$. Moreover, the A.K.-theory is incorrect⁸⁹⁾. The resistivity of Loram's 0.04 and 0.01 at. % alloys varied as T^2 below 1.0 and 1.3 K respectively. Again T_K , this time determined by means of Nagaoka's expression (1.7) decreased with increasing Fe-concentration. We agree with the concentration-dependence of T_K , but the temperature-dependence below 1 K is much more complicated than Loram et al. were able to observe.

Of the other transport-properties the magnetoresistance, though interesting, is not very much suitable for the study of the impurity ground-state, apart from its destruction in high fields. Low-field studies ($k_B T, \mu_B H \ll k_B T_K$) are difficult to interpret since the normal positive magnetoresistance (large at small impurity concentrations) is difficult to separate from the, expectedly small, negative impurity-contribution. No magneto-resistance results on Cu-Fe have been published which are of importance to the present discussion.

The qualitative behaviour of the thermoelectric power of 'Kondo-systems' is well known. A positive or negative hump of the order $10 \mu\text{V/K}$ is observed at about the estimated Kondo-temperature¹³). The low-temperature thermopower of Cu-Fe has been studied by Kjekshus and Pearson⁹⁴). Our experimental results for the thermopower of Cu-Fe are in agreement with published data. What is new in our contribution – apart from an improvement in precision – is that we can quantitatively relate thermopower, resistivity, and heat-conductivity results (chapter III).

II. 2.2 Specific heat

Franck et al.⁹⁵) measured the specific heat of Cu-Fe alloys (0.05, 0.1, 0.2 at.%) from 0.4 – 30 K. A concentration-independent maximum in the impurity specific-heat was observed, occurring at a temperature now estimated about $\frac{1}{3} T_K$. We cannot obtain information on the ground-state properties from these measurements because the lowest temperature was now low enough and the lowest concentration was so high that Fe-Fe interactions are still important. Regarding their concentration-dependence the data of Franck et al. fit in well with later experiments by Brock et al.⁹⁷). (see figure II.11).

Daybell et al.⁹⁶) measured the specific heat of Cu-Fe (0.011, 0.038 at.%) down to 40 mK. The temperature-dependence of their results resembled the prediction of Bloomfield and Hamann (fig. I.7) but Brock et al. showed later that this qualitative agreement was observed only thanks to limited precision and Fe-Fe interaction-effects in the results of Daybell et al.. Precise measurement of the specific-heat of Cu-Fe is very difficult. Results proportional to concentration are not obtained until below 100 ppm Fe and in such a case the Fe-impurities contribute less than 20% of the total heat capacity, which itself is small below 1 K. Yet, a precision not poorer than 1% is desirable. Brock et al.⁹⁷) and Triplett and Phillips⁹⁸) performed very precise measurements on the specific heat of Cu-Fe alloys to below 0.1 K. All alloys studied by these authors exhibited different temperature-dependences of the impurity specific-heat. With decreasing concentration they found however a tendency toward $\Delta C_V \sim T$ (formula (I.17)). Observed deviations from this relation were thought to arise from Fe-Fe interaction-effects. Additional measurements of the specific heat in magnetic fields up to 38 kOe proved this suggestion to be qualitatively correct. We have observed an interesting similarity between the concentration-dependence of the resistivity and the specific-heat. We will further discuss this relation in section II.7.2.

II. 2.3 Magnetic susceptibility.

Hurd²⁶) measured the susceptibility of dilute Cu-Fe alloys from 6 K up to room-temperature. Fitting to the expression $\Delta\chi = \mu_{\text{eff}}^2/3k_B(T - \theta)$ he obtained a Curie-Weiss θ of – 32 K and an effective moment of $3.68 \mu_B$ from which a spin-value of nearly 3/2 was deduced. At lower temperatures (down to 0.4 K) Chaikin and Jensen⁹⁹) measured a higher susceptibility than obtained if Hurd's Curie-Weiss fit is extrapolated. In particular, at the lowest temperatures $\Delta\chi \approx \mu_{\text{eff}}^2/3k_B(T + 16)$.

Daybell and Steyert⁵¹) performed susceptibility measurements down to 40 mK in very small magnetic fields using a mutual-inductance bridge. In their first publication³⁷) the susceptibility of a 110 ppm alloy could be represented by $\Delta\chi = (2.52/(T + 14) + 0.168/(T + 0.045)) \times 10^{-8}$ e.m.u./g ppm Fe. In view of Chaikin and Jensen's work (which was published later however) one might think of two contributions, one by iron and one by another impurity, present in a small amount, with a lower T_K -value. In later work Daybell and Steyert⁵¹) could fit their results to a $T^{-1/2}$ -dependence, and the susceptibility of three concentrations (54, 145, 330 ppm) scaled roughly with concentration, when represented in this way. The fit to $T^{-1/2}$ had its origin in Anderson's theory⁷¹), suggesting such a temperature dependence. Now that Anderson has abandoned his ground-state theory we may think of a different interpretation. Daybell and Steyert's precision apparently allowed both a fit to $T^{-1/2}$ and a fit with two Curie-Weiss temperatures. Besides, they observed a peculiar sensitivity to small external magnetic fields. In fields above 1000 Oe the $T^{-1/2}$ -contribution was almost completely quenched. This is not what can be expected from a spincompensated state with $T_K \approx 20$ K. Since Fe is not very well soluble in Cu it is reasonable to assume the presence of ferromagnetic iron particles (clusters). This was suggested by Golibersuch and Heeger¹⁰⁰), who observed an anomalous low-field dependence of the Cu^{63} nuclear magnetic resonance line-width, saturating in about 2000 Oe at 1.2 K. Such a low-field saturation can only occur if the magnetic particles have a fairly large magnetic moment. According to Golibersuch and Heeger 1% of the total number of Fe-atoms, precipitated in the form of clusters each containing 30 atoms with a magnetic moment like in bulk Fe, could explain their results. In that case however, the $T^{-1/2}$ -term in the susceptibility as measured by Daybell and Steyert would have saturated in fields much lower than 1000 Oe. At very low temperatures a saturation in 1000 Oe would rather be in agreement with a Curie-Weiss $\theta \approx -0.045$ K, as originally proposed by Daybell and Steyert, if this θ is interpreted as the Kondo-temperature of non-isolated Fe-atoms.

Recent magnetization measurements by Tholence and Tournier¹⁰¹) at temperatures from 1.3 – 33 K and magnetic fields up to 70 kOe also showed the presence of particles with an apparently lower T_K than is assumed for isolated Fe. In the analysis of their results Tholence and Tournier assumed two types of impurities to be present: isolated Fe-atoms with concentration c_1 , and Fe-pairs (not necessarily nearest neighbours) with concentration c_2 . The magnetization of the isolated Fe-atoms is proportional to external field up to nearly 70 kOe, proportional to c_1 and can be represented by a Curie-Weiss relation with $\theta = -29$ K and an effective moment of $3.4 \mu_B$. This amounts to an extrapolation of Hurd's results²⁶). The pair-contribution saturates rapidly at 1.3 K and is proportional to c^2 up to $c = 600$ ppm Fe. In this latter case the effective moment corresponds to twice the spin of an isolated Fe-atom and the Curie-Weiss temperature may be 0 to -5 K. If the analysis is correct, half of the low-temperature susceptibility measured by Chaikin and Jensen⁹⁹) arises from non-isolated Fe-atoms. But then it is not easy to understand that the latter authors observed the susceptibility to scale with impurity-concentration (60, 400 ppm).

The observed c^2 -dependence indeed suggests an interaction-effect. Iron-atoms within a certain distance from each other apparently interact in such a

way as to form a magnetic pair with a T_K considerably lower than for isolated Fe. (see also the discussion in section II.6). Tholence and Tournier obtained the relation $c_2 = 130 c^2$. This apparently excludes superparamagnetic clusters as proposed by Golibersuch and Heeger¹⁰⁰). On the contrary, the anomalous low-temperature susceptibility may have a purely statistical origin. Our low-temperature resistivity results to some extent support this point of view.

The present state of knowledge regarding the susceptibility of Cu-Fe is that the impurity-susceptibility of an isolated Fe-atom at $T = 0$ is of order $\mu_{\text{eff}}^2/3k_B T_K$ (μ_{eff} is obtained from a high-temperature Curie-Weiss fit). How this low-temperature value is approached is not known. Curie-Weiss relations used to analyse experimental results are purely empirical and cannot answer this question.

II.2.4 Mössbauer-effect

The results obtained by Frankel et al.⁵³) have been mentioned in section I.6. The same authors discussed the same data in a slightly different way in another paper¹⁰⁴). The essential point in the discussion is a high-temperature and high-field fit of the measured hyperfine-field to a spin-3/2 Brillouin-function. A saturation hyperfine-field per Fe-spin of 80 kOe was obtained in this way as well as an estimate of the field necessary to destroy the spin-correlations about the Fe-atom. The inferred value of H_{sat} was criticised by Golibersuch (see section II.2.5). Recently an analysis of Mössbauer-spectra taken at 'magnetically ordered' Cu-Fe alloys (0.2 - 1.1 at.% Fe) was published by Window¹²²). According to this author H_{sat} at the nucleus of an Fe-atom without nearest Fe-neighbours is 80 kOe. This value is in agreement with Frankel's. Window's analysis is probably not sufficient to settle the point however, even though the derived probability-distribution for the hyperfine-field may be correct. The Fe-atoms in the concentrated alloys have been driven magnetic by interaction with other Fe-atoms and one does not know what will happen to H_{sat} in this case, compared to the case when the magnetism is recovered by an external magnetic field.

II.2.5 Nuclear magnetic resonance and relaxation

a. Demonstration of singlet state for $T \ll T_K$

Extensive investigations have been performed by Heeger and coworkers. Heeger et al.¹⁰²) measured the low-temperature ($T < 1$ K) linewidth of the Cu^{63} nuclear resonance of four Cu-Fe alloys (180, 410, 610, 710 ppm Fe). The linewidth in excess of pure Cu could be represented by $\Delta H = \Delta H_0 + \Delta H_S$. ΔH_S is proportional to the applied magnetic field and roughly proportional to impurity concentration. Furthermore, $\Delta H_S/H$ scales with the impurity susceptibility, which the authors assumed to be proportional to $1/(T+14)$ by comparing known experimental data with each other. Apparently, ΔH_S is proportional to $\langle S_z \rangle$. Since the spin-polarization of the electron-gas is known to be of the RKKY-form above T_K , it follows that also below T_K the

RKKY-oscillations are present, but reduced in the manner in which $\langle S_z \rangle$ is reduced. Linear extrapolation of the observed ΔH gave a residual width ΔH_0 , increasing with concentration, roughly proportionally to $c^{1.5}$. The residual width is apparently due to some interacting Fe-atoms which acquired a magnetic moment. We estimate the residual linewidth of the 410 ppm alloy to correspond to the presence of about 25 ppm particles with Spin=3. This is in agreement with the relation of Tholence and Tournier: $c_2=130 c^2$ (101). If the residual width is accounted for in this way it is clear that the isolated Fe-impurities are in a singlet state at $T=0$. A comparison with Cu-0.025 at.% Mn clearly showed the difference between the low-temperature spin-correlations in the Kondo-effect and short-range magnetic order: the Cu linewidth in Cu-Mn was independent of applied magnetic field (102).

b. Possibility of a large coherence length

The Appelbaum-Kondo model (106) for the ground-state of a magnetic impurity in a metal was worked out by Heeger et al. (102) to calculate the susceptibility and the conduction-electron spin-polarization. In the A.K.-model the ground-state is formed by the impurity-moment, coupled to a many-electron quasiparticle to form a singlet. The quasiparticle has a very long range in space, of the order of the coherence-length, $(2/k_F) (E_F/k_B T_K)$. The finite zero-temperature susceptibility calculated by Heeger consisted of two equal parts, contributed by the local moment and by the quasiparticle. The conduction-electron spin-polarization also consists of two parts: the RKKY-term proportional to $\langle S_z \rangle$ of the local moment and a very long-range positive definite term proportional to $\langle s_z \rangle$ of the quasiparticle. The first term produces oscillatory Knight-shifts at the Cu nuclei, resulting in line-broadening. The main effect of the second term is a Knight-shift in excess of the usual Knight-shift due to the Pauli-paramagnetism. Heeger applied his calculation to Knight-shift measurements on Au-V by Narath et al. (107) and obtained reasonable agreement with experiment. He considered this to be the first indirect measurement of the coherence length in the magnetic-impurity problem.

c. Concentration dependence of the Cu⁶³ nuclear relaxation time

The Cu⁶³ nuclear relaxation-time T_1 was measured by Welsh et al. (108). $1/(T_1 T)$ was found to be constant from 0.07 to 0.3 K but to increase rapidly with concentration, proportionally to c^2 . According to the authors Fe-atoms carrying a magnetic moment by interaction through exchange-fields apparently greater than $k_B T_K / \mu_B$ would fluctuate at very high frequencies and would not contribute to the relaxation-rates. Hence it was suggested that the many-electron ground-state itself would be affected. The conduction-electron singlet pairing function occurring in the theory of Heeger and Jensen (109) gives as the probability P that an electron at the Fermi-surface is paired with one impurity, $P \approx (T_F) / T_K N$ where N is the total number of electrons. So if $cNP=1$ all electrons are coupled to some impurity and if $cNP > 1$ i.e. $c > T_K / T_F$ the ground-state electron-correlations must be disturbed. For Cu-Fe this critical

concentration is about 0.02 at.% (section I.9.). Nagaoka's theory^{31,110}) also predicts such a critical concentration. We will further discuss this problem in section II.6. No other experimental results on Cu⁶³ relaxation-rates in Cu-Fe have been published. We believe, however, that the interpretation of the increase in $1/T_1T$ with concentration is of importance in relation to other NMR-experiments on Cu-Fe.

d. Possible existence of a many-electron quasiparticle in the Appelbaum-Kondo sense.

Golibersuch and Heeger^{100,111}) investigated in detail the temperature- and magnetic field-dependence of the excess Cu⁶³-NMR linewidth in Cu-0.048 at.% Fe. They were guided by the Appelbaum-Kondo ground-state theory, in which half of the susceptibility is localized at the impurity-site and half is due to a quasiparticle spread out in space. Their aim was to verify the existence of an extended quasiparticle. The analysis is independent of the A.K.-model, so that the conclusions are not affected by its failure⁸⁹). Golibersuch first analysed measurements of the Mössbauer-effect of Fe⁵⁷. He assumed the hyperfine-field at the Fe-nucleus to be proportional to the local magnetization, i.e. $\sim \langle S_Z^{Fe} \rangle$, which is reasonable in view of what is known both experimentally and theoretically about hyperfine-fields in metals. Golibersuch noticed that the hyperfine-field at the Fe-nucleus is proportional to $H/(T+32)$, which above 17 K is proportional to the static bulk susceptibility²⁶). A saturation hyperfine-field per Fe-spin of 141 kOe was obtained, which is much larger than the value of Frankel et al.⁵³). The discrepancy was attributed by Golibersuch to the fact that only at very high temperatures ($T \gg T_K$) the Fe-magnetization may be expected to follow a Brillouin-function. If the actual magnetization is smaller than the corresponding free-spin value, a fit to a Brillouin-function automatically leads to an underestimate of the saturation hyperfine-field.

By extrapolation, also at lower-temperatures the Fe⁵⁷ hyperfine-field appeared to be proportional to $H/(T+32)$ and it was therefore concluded that at all temperatures and fields $\langle S_Z^{Fe} \rangle$ is proportional to $H/(T+32)$ i.e. the local susceptibility. A perturbation-theoretical calculation of χ was shown to be represented within 1/2 % by $\chi = (\mu^2_{eff}/1.22)/3 \text{ kB} (T+4.5T_K)$ in the range $7 \leq T/T_K \leq 100$. This yields $T_K = 7.1 \text{ K}$. According to Daybell and Steyert⁵¹), if the anomalous $T^{-1/2}$ -term is not taken into account, the total susceptibility below 1 K is $\mu^2_{eff}/3 \text{ kB} (T+16)$, i.e. twice the local susceptibility. Golibersuch obtained the total susceptibility between 1 and 20 K by interpolation. The measurements by Chaikin and Jensen¹⁰⁹) later confirmed that below 10 K: $\chi = \mu^2_{eff}/3 \text{ kB} (T+16)$. By scaling the hyperfine-field and linewidth measurements at high temperatures and magnetic fields, it turned out that below 20 K $\langle S_Z^{total} \rangle/H$ as measured by the linewidth and scaling with the bulk susceptibility, increased above the local $\langle S_Z^{Fe} \rangle/H$. This was interpreted as the building-up of the quasiparticle. If at low temperatures ($T \ll T_K$) the external magnetic field was increased $\langle S_Z^{total} \rangle$ increased twice as rapidly as $\langle S_Z^{Fe} \rangle$, in agreement with the ratio of the susceptibilities. At about 50 kOe $\langle S_Z^{total} \rangle$ and $\langle S_Z^{Fe} \rangle$ are equal. This was interpreted as a destruction of the quasiparticle at fields above 50 kOe. Taking the estimate $T_K = 7.1 \text{ K}$ the

quasiparticle would be destroyed at $3 T_K$, or at a field of $H_c = k_B T_K / 2 \mu_B$. So the quasiparticle would be destroyed in regions of temperature and field where spin-correlations about the impurity are still important.

e. Extension in space of the quasiparticle for Cu-Fe

Golibersuch^{111,112}) also attempted to measure the range in space of the quasiparticle. Long-range spin-correlations had been predicted by several authors^{31, 102}). A positive definite spin-polarization would cause an extra Knight-shift at the Cu⁶³ nuclear resonance. The estimated Knight-shift was much larger than observed and the quasiparticle should thus be confined to a region of space at least within 9 Å from the impurity. (The resonance of Cu nuclei within that region is 'wiped out' because of the large amplitude of the spin-polarization near to the impurity). This conclusion is independent of the actual space-dependence of the spin-polarization, but *does* depend on the assumption that the contribution of the quasiparticle to the total spin-polarization is equal to the contribution of the local susceptibility. An additional proof of the localized nature of the quasiparticle was provided¹¹¹) by the decrease of $\langle S_z \rangle / H$ upon addition of Al (up to 9 at.%) to Cu-Fe, which limits the electron mean free path. This decrease was much smaller than one might expect if a very long-range spin-polarization were present.

The picture of the ground-state of Fe in Cu as developed by Heeger et al¹⁰²) and Golibersuch and Heeger¹⁰⁰) is very elegant, but various experimental questions remain.

1. The Fe-concentration of 0.048 at.% is not very low. Welsh et al.¹⁰⁸) found the Fe-contribution to $1/T_1 T$ for this alloy to be a factor of at least 2 higher, as compared to a 0.018 at.% alloy, than if proportionality to the concentration is assumed.
2. The NMR-linewidth scales with the bulk susceptibility as measured by Chaikin and Jensen⁹⁹). Tholence and Tournier¹⁰¹) however, conclude from magnetization measurements that the susceptibility of isolated Fe-atoms is proportional to $1/(T+29)$, even at 1 K. Thus Chaikin and Jensen's and also Golibersuch and Heeger's results below 50 kOe would contain a contribution of interacting Fe-atoms, which is not completely accounted for by the low-field ($H < 2000$ Oe) dependence of the linewidth. On the other hand, it would be quite remarkable if the Fe-susceptibility were proportional to $1/(T+30)$ from 1 K up to 300 K.
3. The experimental magnetic field-dependence of $\langle S_z^{\text{loc}} \rangle$ in the region where the quasiparticle is not yet broken up rests upon three points taken from Mössbauer-effect measurements by Kitchens et al.³³). Inspection of these data raises the question if their precision justifies the conclusions drawn by Golibersuch and Heeger.
4. Recent specific-heat results⁹⁸) and our own resistivity-measurements (section II.6) show that at a concentration of about 500 ppm Fe, Cu-Fe is by no means a dilute alloy anymore.

Recently, Narath¹¹³) reviewed a number of results on the impurity nuclear

magnetic resonance of dilute alloys such as Al-Mn, Au-V and Mo-Co. According to Narath the observed Knight-shifts, nuclear relaxation-rates and linewidths can be interpreted on the basis of a Friedel-Anderson model of a non-magnetic virtual-bound state. Thus a Hartree-Fock treatment of the electronic correlations would suffice and no many-electron quasiparticle would exist, contrary to Heeger's analysis of Au-V. In view of the remarks made above it is not impossible that Cu-Fe will join the set in the near future. In this context recent neutron-diffraction experiments by Stassis and Shull¹¹⁴) should be mentioned. These authors measured the temperature-dependence of the local Fe-magnetization in a Cu-1000 ppm Fe single-crystal at 15 kOe. They observed the local magnetization to scale with the bulk susceptibility. This would provide an additional argument against the quasiparticle concept, were it not that 1000 ppm is a rather high concentration, so that probably more than 10 % of all Fe-atoms will be magnetic or nearly magnetic and will contribute appreciably to the magnetization.

II.3. Experimental details

II.3.1. Alloy-preparation

All copper alloys were melted in quartz in high vacuum ($<10^{-5}$ Torr) in an Edwards radiation furnace. Pure ASARCO-copper (99.999 + at.%) was first melted, degassed and heavily etched after solidification. A Cu-0.1 at. % Fe master alloy was prepared (Fe from Johnson and Matthey, no. 27967) and was used to prepare all the other alloys. After melting the alloys were homogenized just below the melting point, and were subsequently quenched in water. After etching, appropriate pieces were spark cut from the alloy, etched, rolled to about 0.6 mm diameter, etched again and drawn through carefully cleaned diamond dies to a diameter of 0.1 mm for alloys up to 200 ppm Fe and somewhat larger diameters for the more concentrated alloys. Wire lengths varied from 50-350 cm. After drawing each wire was annealed to remove strains, and to reduce the contribution of lattice-defects to the resistivity. The annealing was performed in vacuum, in a quartz tube, in which a quartz cylinder was suspended, on which the wire was wound. After annealing the wire was cooled by letting Argon gas into the quartz tube, and water around it. This procedure provided reasonably fast cooling – although not really rapid quenching – while the wires were kept fine.

Figures regarding annealing times and temperatures, etc. are given in

Table II.1

Alloy ppm Fe nominal	melting time (hours)	1000 °C homog. (hours)	Annealing after drawing		$\Delta\rho(T=0)$ $\mu\Omega$ cm	$\Delta\rho/c_{\text{nom}}$ $\mu\Omega$ cm/at. %	analysis at. ppm	$\Delta\rho/c_{\text{an}}$ $\mu\Omega$ cm/at. %
			hours	°C				
Cu	2	—	3.5	700	0.00214	—	<1	—
30	2	24	10	700	0.03690	12.3	29.0	12.7
50	1.5	24	4	700	0.05697	11.4	51.0	11.2
100	2	24	4.5	700	0.1194	11.9	98.0	12.2
200	2	24	4.5	700	0.2266	11.3	182	12.5
500	1	24	4.5	800	0.6043	12.1	421	14.4
460?	0.5	—	2	850	0.528	—	560	9.4
1000	3	45	5	800	1.110	11.1	754	14.7

Table II.1. $\Delta\rho$ is the resistivity of the alloy minus that of pure copper. For copper the measured resistivity is given. It is seen that the nominal concentrations are in reasonably good agreement with the analysis, which is confirmed by the resistivities at $T=0$. The larger errors in the highest three concentrations must originate from the method of analysis (atomic absorption), since all nominal concentrations scale well with $\Delta\rho(T=0)$.

II.3.2. Resistivity measurements

Electrical resistivities were measured by the four-terminal method. Potential leads taken from the sample-wire were spot-welded to the ends of it. The potential drop across the sample was compared to the potential drop across a standard resistor, using a six-dial Guildline potentiometer. Ultra stable current supplies (≈ 1 ppm) provided the sample- and potentiometer-currents. The null-detector was a Keithly model 147, used on its $0.3 \mu\text{V}$ full-scale range. This scale was an optimum choice in view of the circuit noise and because on more sensitive scales the null-detector has a rise time exceeding 1 sec.. Thermal voltages in the circuit were compensated by means of the zero-suppress. The potentiometer-dials were set such that when the currents were commutated the meter moved from one side of the centre-zero to the other side. The unbalance of the meter was read using a digital voltmeter connected to the output terminals of the null-detector. For each resistance-measurement the sample- and potentiometer-currents were electrically commutated about 100 times. In this way a resolution of about 1.5×10^{-9} Volt was achieved. Typical sample-resistance and current-values are 0.2Ω and 0.4 mA . Thus a relative precision of 1 in 50,000 is attained in the resistance-measurements, while dissipating 0.3 erg/sec. of Joule heat. This is not a very small amount at temperatures of 50 mK . The thermal contact between sample and sample-holder is therefore of particular importance if our precision is to be meaningful. The specimen-wire was mounted in the following way. The outer surface of a thin-walled (0.2 mm) copper cylinder of about 3 cm length and 1 cm diameter was covered with a sheet of cigarette paper (25μ) soaked in Apiezon-N grease. The sample-wire and a silk thread were wound upon the copper cylinder next to each other and a reliable insulation of the copper windings was achieved in this way. The inner surface of two thin-walled copper half cylinders was insulated in the same way as the cylinder mentioned above. The length was the same but the inner radius was 0.15 mm larger than the outer radius of the first cylinder. The cylinder with the wire wound upon it was then covered with the two half cylinders and everything was soaked in Apiezon-N grease and held firmly together by pieces of elastic. In this way a good thermal contact was obtained between the wire and the cylinder. Copper braids, soldered to the inner and outer cylinders thermally connected them to each other and to the cooling salt. We checked the thermal contact by measuring the resistivity with two different currents (factor 2 in energy dissipation) and found no difference outside the experimental accuracy.

The absolute accuracy of the resistivity-values is determined by the measurement of the wire-diameter. The wires were round within the accuracy

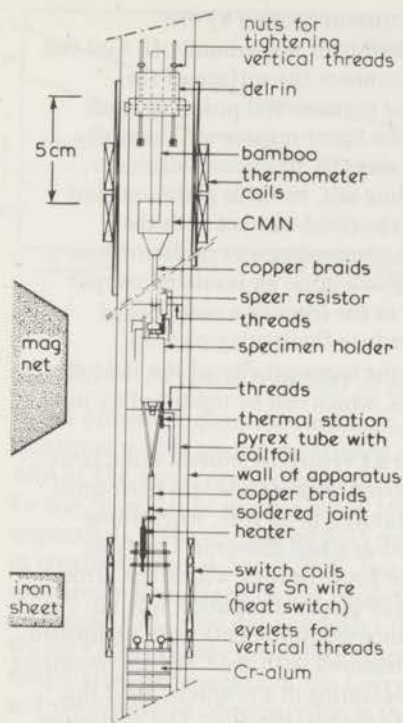


fig. II.1. Part of the apparatus. Not shown are the niobium wires for electric contact and the vertical threads, tightened to prevent any movement of the specimen-holder.

of the measurement. Diameters were measured with a micrometer to an approximate accuracy of 1μ , so that the error in the shape-factor of the alloys up to 200 ppm Fe is 2%. In many analyses however, the resistivities were normalized by their zero-temperature value and then the accuracy of derived data is much better.

II.3.3 Cryo-techniques

The specimen-holder is suspended in a glass apparatus of a design common in the Kamerlingh Onnes Laboratory. The most important part is shown in figure II.1. Temperatures above 1 K are achieved with the apparatus surrounded by liquid He⁴ and containing He⁴ exchange-gas. Temperatures below 1 K are obtained by adiabatic demagnetization of CrK-alum from 1 K and 22 kOe. The specimen and thermometers are cooled via a pure tin heat-switch, actuated by niobium coils in liquid Helium. When measurements in a magnetic field are performed, the tin-switch is protected against the field by a sheet of iron*), with a circular gap to accommodate the cryostat.

At the bottom the specimen-holder is soldered to copper braids, which are thermally connected to the cooling-salt by the heat-switch. At the top of the specimen-holder a screw-thread is found. The Speer-resistor (220Ω , $\frac{1}{2}$ Watt) is thermally connected to the sample-holder by clamping one of the electric terminals between the sample-holder and a copper nut, which is hard-soldered to the copper braids leading to the CMN (Cerium Magnesium Nitrate) thermometer-salt. The copper nut and the inner cylinder of the specimen-holder

*) We thank Mr. J.N. Haasbroek for the suggestion.

are cut along the vertical axis, to reduce eddy-current heating by the thermometer-coils. The insulation of the Speer-resistor was ground off. Coil-foil and Apiezon-N grease were used to thermally connect the surface of the Speer-resistor to its lower electric terminal. The current- and potential-leads of the specimen and the electrical leads from the Speer-resistor are thermally anchored to the specimen-holder and niobium wires of 50 microns diameter, leading along the cooling-salt, through a shielding-salt, towards platinum-glass seals, at the bottom of the apparatus, provide electrical contact with the measuring equipment. The heater consists of a constantan wire of 30 microns diameter, total resistance 800 Ω , wound and glued upon an insulated copper wire of 1 mm diameter. Since the specimen is in the form of a coil, special care was taken to fix the specimen-holder to reduce fluctuating pick-up voltages, when measuring in a magnetic field (the homogeneity of the field was only 10% along the specimen), Cotton threads, which can be tightened by nuts, are used to fix the specimen-holder.

The CMN-susceptibility was measured with a Cryotronix mutual-inductance bridge. Calibration against the liquid He⁴ vapour-pressure scale was performed in the usual way. The Speer-resistance was measured in an A.C. Wheatstone-bridge (33 Hz) and a lock-in amplifier was used as a null-detector. Care was taken to keep the decrease of resistance due to Joule heating within the error of the measurement. Above 0.3 K the maximum power dissipation was 10^{-11} Watts, below 0.3 K 10^{-13} Watts. When resistance measurements were performed in zero magnetic field, the temperature was measured with the CMN-thermometer and the Speer-resistor was calibrated. When measuring in a magnetic field the calibrated Speer-resistor was used to determine the temperature. The maximum applied magnetic field was 2000 Oe. According to Mess¹⁶⁾ the magneto-resistance of a Speer-resistor in a field of 2000 Oe is 0.5% at 0.23 K and 3.5% at 0.11 K. The relative error in the temperature, if we use the zero-field calibration, is of the same magnitude and can be neglected for our purpose. A discussion of Speer-resistance thermometry below 1 K can be found in the thesis by Mess¹⁶⁾. We estimate a maximum error in the temperature of 0.5% below 1 K, which is mainly determined by the error in the calibration of the CMN-thermometer. Below 0.3 K we estimate a maximum error of 1% in T. The Wheatstone-bridge was less sensitive at these temperature because of the requirement of low power-dissipation. To these errors should be added the error caused by the use of the zero-field Speer-calibration in 1000 and 2000 Oe. This last error can be neglected above 0.5 K.

II.4. Pure copper

In this section we discuss the resistivity of pure copper. This is important because we want to determine the temperature-dependence of the resistivity of very dilute Cu-Fe alloys and the presence of other magnetic impurities in the pure copper host may influence the result. In fig. II.2 we show the resistivity of pure copper from 0.05 K up to 4.2 K, in zero-field and in 1000 Oe. We notice that $d^2\rho/dT^2$ is positive. This is not what we expect for an iron impurity namely $d^2\rho/dT^2 < 0$ (fig. I.5). The American Smelting and Refining Company supplies a standard spectrographical analysis report, according to which Fe and

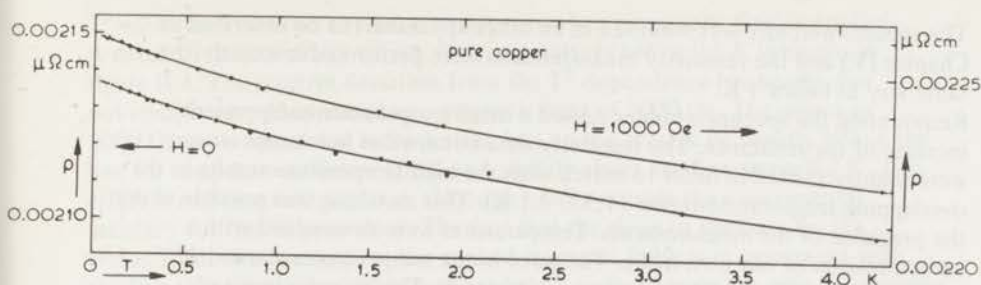


fig. II.2. Electrical resistivity of pure copper. (ASARCO, 99.999 + at.%)

Cr are present in quantities less than 0.7 and 0.5 ppm respectively. Other transition metals are not mentioned. Hurd¹¹⁷) quotes an analysis of pure ASARCO-copper, performed at the National Research Council, Ottawa. Only Fe was found (0.35 ppm), Co and Mn were not visible (< 0.5 and < 0.1 ppm respectively). The number of 0.35 ppm Fe is not inconsistent with the increase in resistivity from 4.2 to 0.05 K, but the curvature is wrong. Our pure copper specimen was analysed by the Analytical Laboratories of Johnson Matthey Chemicals Ltd., who did not detect the presence of any transition elements. We see Cr as the only possibility (this may even be in agreement with the temperature-dependence of the Lorenz-number of pure copper; see ref. 139) and the estimated concentration is then 0.05 ppm Cr¹¹⁸). It is also possible that both Cr and Fe are present. Anyway, only Cr and Fe can explain the fact that in 1000 Oe only a parallel shift of the resistivity curve is observed.

(T_K of Cu-Fe is about 20 K, of Cu-Cr about 2 K). If Mn were present the curvature of the resistivity-versus-temperature curve would change in a magnetic field of 1000 Oe. Partly the observed resistivity value may be caused by lattice-defects, introduced during the mounting of the specimen, and partly it may be caused by boundary-scattering. The residual resistivity of a pure-copper rod is a factor of two smaller, although the same type of temperature dependence ($d^2\rho/dT^2 > 0$) is observed (see ref. 139) as in the wire under discussion.

We subtracted the resistivity of pure copper from the resistivity of the Cu-Fe samples. In the present case of temperature-dependent resistivities one then has to be aware that deviations from the so-called Matthiessen's rule will occur. In Appendix I to this chapter we will show that these deviations do not affect our conclusions and can be neglected below 1 K.

II.5. Copper-50 ppm iron

We devote one section to our 50 ppm alloy. The behaviour of the resistivity is not essentially different from the other concentrations, but in this particular case we performed measurements up to 16.5 K to a very high precision. We want to draw some conclusions which cannot be drawn from the other measurements, since they were not performed above 4.2 K and mostly only below the lambda-point of Helium. We measured both pure copper and Cu-50 ppm Fe up to 16.5 K. This was done after the measurements below 1 K.

The specimen-holder was mounted in an other apparatus (to be described in Chapter IV) and the resistivity measurements were performed in exactly the same way as below 1 K.

Remounting the specimen-holder caused a small temperature-independent increase of the resistance. The resistivity data obtained at low temperatures were slightly shifted in order to match with the high-temperature results in the overlapping temperature-region (1.3 – 2.1 K). This matching was possible within the precision of the measurements. Temperatures were determined with a carbon-resister of our own make. The error in the temperatures above 1 K is estimated 2 mK or 0.05 % whichever is larger *). The manufacture and calibration of these carbon-thermometers have been described extensively in a paper by the present author¹⁴⁶).

The resistivity results below 1.3 K are shown in fig. II.3. Undoubtedly, the temperature-dependent part of the resistivity is proportional to T^2 below 1 K. A small positive deviation from the T^2 -dependence may be observed below

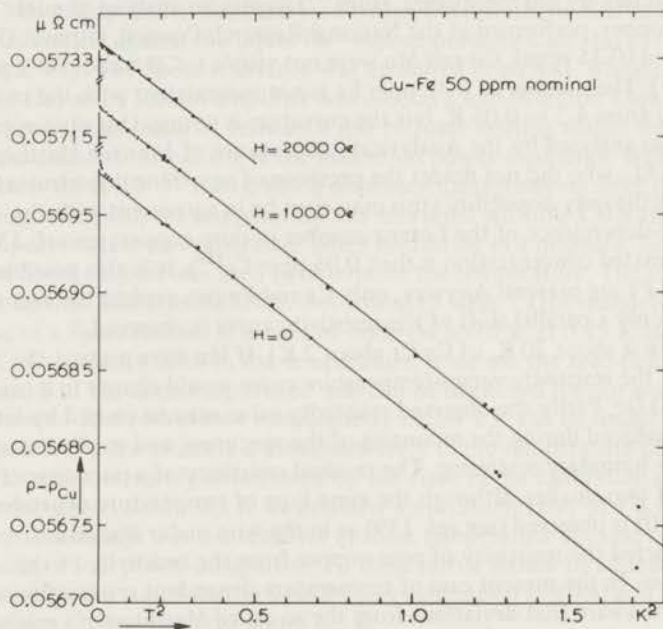


fig. II.3. Electrical resistivity $\Delta \rho = \rho - \rho_{Cu}$ of a 50 ppm Cu-Fe alloy versus T^2 below 1.3 K in magnetic fields $H=0, 1000$ and 2000 Oe. It should be noted that there is no logical relation between the zero-temperature resistivities ($\Delta \rho H \sim H^2$ for example). This is because the specimen was sometimes warmed up to room-temperature between two sets of measurements. This results generally in a temperature-independent shift of the resistivity. We never observed a change in the temperature-dependence of the resistivity after thermal cycling to room-temperature.

*) Possible errors in the Helium and Hydrogen vapour-pressure scales are not taken into account.

$T^2=0.1$ for $H=0$. This deviation disappears when a magnetic field is applied. A detail of the resistivity-curves, for temperatures below 0.5 K is shown in figure II.4. The positive deviation from the T^2 -dependence has nearly, but not completely, disappeared in a magnetic field of 1000 Oe. The points in 2000 Oe show somewhat more scatter, but on the average lie slightly below the line for temperatures below 0.2 K and slightly above the line above 0.2 K. The effect is real (see next section), although hardly outside the experimental accuracy for the 50 ppm-alloy. The fact that the slope of the lines for $\Delta\rho$ versus T^2 does not change in the applied magnetic fields is in agreement with the fact that more than 200 kOe is needed to really destroy the spin-correlations about the Fe-impurities (section I.6). One may expect the effects of field- and

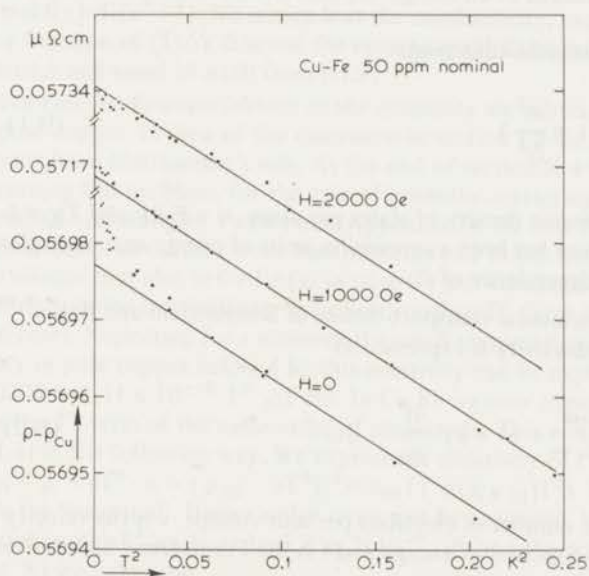


fig. II.4 Detail of fig. II.3, for temperatures below 0.4 K. The straight lines were drawn exactly parallel to the corresponding lines in fig. II.3.

temperature-variation to be independent of each other¹¹⁹) in first approximation, i.e. $\Delta\rho = \alpha (T/T_K)^2 + \beta (H/H_K)^2$ where α and β are of order -1 and H_K is a critical magnetic field, necessary to destroy the spin-correlations about Fe. The disappearance of the low-temperature positive deviation from the T^2 -dependence in small magnetic fields suggests that it is caused by magnetic particles with a low Kondo-temperature. In the next section we shall show that these particles are most probably interacting iron-atoms. We shall also show in the next section that the resistivity contribution of these particles is proportional to the logarithm of the temperature. In the 50 ppm-alloy this contribution is very small and we only observe it because the T^2 -term is negligible from 0.05 to

0.2 K, while the $\ln T$ -term varies rapidly. We shall subtract the small $\ln T$ -term and further discuss what we believe is the contribution to the resistivity of non-interacting iron-atoms.

II.5.1. An empirical relaxation-time

The results of Nagaoka (formula I.7) will guide us in the analysis. In Chapter I we quoted the work of Hamann, who showed Nagaoka's derivation to be incorrect. We conclude from our results however, that a transport relaxation-time of the form given by Nagaoka apparently describes the experimental results. The same remark can be made regarding other theories predicting a T^2 -term in the resistivity (this does *not* apply to alloys of the Pd-Ni type because the essentially zero-resistivity at $T=0$ precludes a description of the resistivity by means of an energy-dependent relaxation-time; see however also section III.5).

Nagaoka's relaxation-time reads:

$$\tau = \frac{\pi \rho_1 \hbar}{2c} \left(1 + \frac{\omega^2}{\Delta^2} \right) \quad (\text{II.1})$$

ρ_1 is the electronic density of states per atom, $\omega = E - E_F$ and $T_K = 1.14 \Delta$. The temperature has been expressed in units of energy and we neglect the temperature-dependence of Δ .

In the semiclassical transport-theory of Sommerfeld and Bethe^{7,20}) the electrical conductivity is expressed as

$$\sigma = -\frac{2}{3} n e^2 \int_{-\infty}^{+\infty} v^2 \tau \rho_1 \frac{\partial f}{\partial \omega} d\omega \quad (\text{II.2})$$

where n is the number of electrons per unit volume, v is the velocity of the electrons as a function of energy and f is the Fermi-Dirac distribution-function. $\frac{\partial f}{\partial \omega}$ is nearly a δ -function for $k_B T \ll E_F$. If we substitute (II.1) into (II.2) we see that near $\omega = 0$ only ω^2 is varying rapidly relative to its value at $\omega = 0$. The other quantities, like ρ_1 are proportional to powers of the total kinetic energy and thus vary slowly with respect to their value at $\omega = 0$. We can take them all out of the integral and obtain

$$\sigma = -\frac{n e^2}{m} \frac{\pi \rho_1 \hbar}{2c} \int_{-\infty}^{+\infty} \left(1 + \frac{\omega^2}{\Delta^2} \right) \frac{\partial f}{\partial \omega} d\omega \quad (\text{II.3})$$

Applying the familiar Sommerfeld-expansion, the term containing ω^2 is seen to result in a T^2 -term for the electrical conductivity. We now want to develop an empirical relaxation-time which can be used to analyse our resistivity data above 1 K. We observe:

- 1 That σ increases as T^2 from its zero-temperature value.

2. It is assumed and experiments support this⁶⁵), that for $T \gg T_K$ the resistivity becomes temperature-independent again. In fact our resistivity-curve for Cu-50 ppm Fe shows an inflection point at $T \approx 5$ K.

If we replace ω^2/Δ^2 in (II.3) by $\omega^2/(\omega^2 + \Delta^2)$ the behaviour for $T \ll \Delta$ does not change. Taking ω/T as a new variable it is easily seen however that σ does not increase to infinity like (II.3), but attains a high-temperature constant value. In order to analyse numerically our results we add a few more terms, of the form $\omega^{2n}/(\omega^{2n} + \Delta^{2n})$ and write

$$\frac{\sigma(T) - \sigma(0)}{\sigma(0)} = - \sum_{n=1}^m C(n) \int_{-\infty}^{+\infty} \frac{(xT/\Delta)^{2n}}{(xT/\Delta)^{2n} + 1} \frac{\partial f}{\partial x} dx \quad (II.4)$$

where $\omega = xT$ and $f(x) = 1/(e^x + 1)$. We notice that the conductivity, expressed in this way is a function of (T/Δ) . Δ is not the same as in (II.3) because $\sigma(0)$ from experiment is not equal to $\sigma(0)$ from (II.3).

In order to obtain the Fe-contribution to the resistivity we subtracted the resistivity of pure copper. In view of the discussion in section I.4 we have to expect deviations from Matthiessen's rule. At the end of section II.4 we made a remark concerning this problem, for the case of potential-scattering, interfering with the anomalous scattering by Fe (see also Appendix I). We now have to consider the problem of deviations from Matthiessen's rule in the lattice-resistivity. We assume that also in Cu-Fe (as in pure Cu and Cu-Sn; section I.4) the lattice-contribution to the resistivity is proportional to T^5 (This is not necessarily the case). Neglecting for a moment the small temperature-dependence of the resistivity in pure copper below 4 K, this resistivity can be expressed as $\rho_{Cu} = 0.00208 + 2.41 \times 10^{-10} T^5 \mu\Omega \text{ cm}$. In Cu-Fe we may expect a coefficient for the T^5 -term of the same order of magnitude. This will be included in (II.4) in the following way. We express the resistivity of Cu-50 ppm Fe as $\rho_m = \rho + aT^5$; $\sigma = (\rho_m - aT^5)^{-1} = \sigma_m (1 + (a/\rho_m)T^5)$. The index m stands for 'measured'. Higher order terms can be neglected, because the maximum value of $(aT^5/\rho_m)^2$ at 16.5 K is 2×10^{-5} , if for a the pure copper value is chosen. So we have now

$$\frac{\sigma_m(T) - \sigma_m(0)}{\sigma_m(0)} = - \sum_{n=1}^m [C(n) \int_{-\infty}^{+\infty} \frac{(xT/\Delta)^{2n}}{(xT/\Delta)^{2n} + 1} \frac{\partial f}{\partial x} dx] + \frac{C(m+1)\rho(0)}{\rho_m^2} T^5 \quad (II.5)$$

This expression was used to analyse the resistivity of the Cu-50 ppm Fe-alloy. For several values of m , resistivity values from 0.05 K up to 16.5 K (164 points) were fitted using a least-squares procedure. The integrals at each temperature were computed using a 24 point Gauss-Laguerre subroutine. The best value of Δ was obtained by iteration for $m=6$. The results are shown in table II.2. We give the data as supplied by the computer. The values of $C(m+1)$ for all three values of m are nearly equal and of the same order of magnitude as for pure copper. A point has been indicated in fig. I.3 to compare with Cu-Sn. The coefficient of T^5 thus derived for Cu-50 ppm Fe is much larger than for Cu-Sn and is comparable to a Cu-Au alloy of the same residual resistivity⁴²). For

Table II.2

Numerical analysis of the resistivity of Cu-50 ppm Fe, using expression (II.5). $\rho(0) = 0.0573692 \mu\Omega \text{ cm}$; $\Delta = 21.25 \text{ K}$; 164 points; 0.05 K – 16.5 K

$m=6$; r.m.s. $\Delta\rho/\rho = 2.3 \times 10^{-5}$	$m=4$; r.m.s. $\Delta\rho/\rho = 2.6 \times 10^{-5}$
C(1) = 3.84817958281E-01	C(1) = 3.81452836846E-01
C(2) = -1.65906161978E-01	C(2) = 9.96232469344E-02
C(3) = 3.49428116602E-01	C(3) = 5.60687263952E-02
C(4) = -5.13272235948E-01	C(4) = 9.04363704945E-03
C(5) = 3.93421030967E-01	C(5) = 3.45071423680E-10
C(6) = -1.19812141474E-01	
C(7) = 3.37609285513E-10	
	$m=2$; r.m.s. $\Delta\rho/\rho = 7.4 \times 10^{-5}$; oscill.
If $\Delta=23.0$, r.m.s. $\Delta\rho/\rho = 3.4 \times 10^{-5}$	C(1) = 3.70724868027E-01
	C(2) = -4.24930305058E-02
If $\Delta=19.5$, r.m.s. $\Delta\rho/\rho = 3.9 \times 10^{-5}$	C(3) = 3.24516444882E-10

$m = 6$ the error in the fit is about the error in the experimental results. The precision of the fit does not change appreciably for $m = 4$ compared to $m = 6$. For $m = 2$ the computed curve oscillates along the measured curve.

In view of the precision of the fit the number of coefficients required is fairly small. Including Δ , only 5 coefficients are needed to obtain an accurate representation of the experimental data (We exclude the last coefficient which only accounts for deviations from Matthiessen's rule). These data are very precise and in view of this we venture some physical conclusions, although we are fully aware of the dangers of drawing conclusions from fitted curves. We have seen in chapter I that various expressions non-analytic in T have been derived theoretically. In fact, almost all expressions derived on the basis of the s-d exchange model contain $\ln T$ as variable. We conclude from our analysis that there is nothing non-analytic in the behaviour of the resistivity, or more generally, of the transport relaxation-time, below T_K . The values of the computed coefficients do not vary arbitrarily, but their absolute value is of equal order of magnitude and their sign alternates in a monotonous way. We believe that our empirical relaxation-time somehow represents the actual situation, i.e. that a correct theory will probably predict a relaxation-time which is a power series in ω/Δ below T_K . Since the value of Δ , obtained by iteration, is very close to the Kondo temperature of Cu-Fe (section II.5.2) also the actual form of the terms in (II.5) may have some bearing to reality. For a simple power-series in ω/Δ the value of Δ is unimportant. A variation in Δ is compensated by a variation in the coefficients.

The empirical relaxation-time can be used to compute the temperature-dependence of the Lorenz-number, which will be done in chapter III. This is one reason for giving our full results in table II.2. Another reason is to facilitate the comparison of our results with others'. One has to be careful however, in making comparisons. We subtracted the pure copper resistivity, which may partly be caused by boundary-scattering. Boundary-scattering is less important

in the Cu-Fe alloys and we may have subtracted too much of pure copper-contribution. The wire-diameter of our dilute alloys was 0.1 mm, while the electronic mean free path in the case of Cu-50 ppm Fe is 2 microns, i.e. 2% of the diameter. We will briefly discuss the possible influence of size-effects on the Kondo-effect in Appendix II to this chapter.

We checked numerically the effect of subtracting too much of pure-copper resistivity, by adding again to all points a constant value, approximately equal to the measured pure-copper resistivity. The precision of the fit to expression (II.5) did not change and the coefficients changed only a few percent. The calculated Lorenz-number decreased less than 0.5% at 10 K.

II.5.2 An empirical t-matrix

We included only even powers of ω in the empirical relaxation-time. Terms containing odd functions of ω do not contribute to the integrals because $\partial f/\partial\omega$ is an even function of ω . Odd powers of ω do however contribute to the thermoelectric power, while even powers do not. Therefore, Nagaoka's relaxation-time gives a zero result for the thermopower. The reason is that only exchange-scattering has been considered. Inclusion of potential-scattering is necessary to explain the 'giant' thermopowers observed in dilute alloys showing the Kondo-effect. We shall introduce the effect of potential-scattering into Nagaoka's relaxation-time in a phenomenological way and devote some more discussion to the resistivity below 4 K. The results obtained for the thermopower and the Lorenz-number using this modified Nagaoka relaxation-time will be discussed in chapter III.

For scattering with a single phase-shift only, the transport properties are determined by the non spin-flip part $t(\omega)$ of the scattering amplitude¹⁷⁾. Nagaoka's result for $t(\omega)$ is

$$t_N(\omega) = \frac{1}{2\pi i \rho_1} \left(1 - \frac{\omega - i\Delta}{\omega + i\Delta} \right) \quad (\text{II.6})$$

The transport relaxation-time is obtained by $\tau(\omega)^{-1} = 2c \text{Im } t_N(\omega)$, where c is the impurity concentration. Potential-scattering may be introduced by means of a potential-scattering phase-shift as follows¹²⁰⁾

$$1 - 2\pi i \rho_1 t(\omega) = e^{2i\delta} (1 - 2\pi i \rho_1 t_N(\omega)) \quad (\text{II.7})$$

and thus

$$t(\omega) = \frac{1}{2\pi i \rho_1} \left(1 - e^{2i\delta} \frac{\omega - i\Delta}{\omega + i\Delta} \right) \quad (\text{II.8})$$

The transport relaxation-time is again obtained from $\tau(\omega)^{-1} = 2c \text{Im } t(\omega)$. Calculation of the thermopower yields for low temperatures (see also chapter III)

$$S = \frac{k_B}{e} \frac{\sin 2\delta}{1 + \cos 2\delta} \frac{2\pi^2}{3} \frac{T}{\Delta} \quad (\text{II.9})$$

This may be a factor of T_F/T_K larger than the normal diffusion thermopower. The electrical resistivity at $T = 0$ obtained with (II.8) or (II.1) has a maximum value of $3.8 \mu\Omega \text{ cm/at.}\%$ for an impurity in copper*. This value corresponds to the maximum scattering of an $l=0$ partial wave. If δ differs from zero, the resistivity at $T = 0$ is smaller, namely $3.8(1 + \cos 2\delta)/2 \mu\Omega \text{ cm/at.}\%$. In the s-d exchange model as used by Nagaoka, Hamann and others, J is an s-wave potential⁴³ so that even for $S > \frac{1}{2}$ Hamann finds at $T = 0$ the s-wave unitarity limit for the resistivity, i.e. $3.8 \mu\Omega \text{ cm/at.}\%$. The resistivity of Cu-Fe at $T = 0$ is nearly equal to $3 \times 3.8 \mu\Omega \text{ cm/at.}\%$. Since the spin of Fe is $3/2$ this would be in agreement with Schrieffer's suggestion⁴³) of $2S \times 3.8 \mu\Omega \text{ cm/at.}\%$ for the electrical resistivity at $T = 0$. This would be valid only for exchange-scattering however. According to Loram⁶⁵) the 'step' in the resistivity from $T = 0$ to $T \gg T_K$ is of the order of $4 \mu\Omega \text{ cm/at.}\%$ so that apparently there is an appreciable potential-scattering contribution to the resistivity in Cu-Fe. According to Daybell and Steyert¹¹⁸) in Cu-Cr the resistivity-step is at least $2.5 \times 3.8 \mu\Omega \text{ cm/at.}\%$. The spin-value of Cr in Cu is estimated $3/2$ ^{98, 121}), like in Cu-Fe.

We clearly cannot account for the resistivity of Cu-Fe on the basis of (II.8). Since the contribution of exchange-scattering, connected with the potential scattering phase-shift 2δ , is smaller than the observed resistivity at $T = 0$ there is probably another potential-scattering contribution, not connected with exchange-scattering. In the picture given by Schrieffer⁴³) this may be caused by doubly occupied orbitals, which cannot exchange-scatter conduction electrons (resonance scattering in Friedel's virtual bound state picture). We propose a modification of (II.8) in the following way

$$t(\omega) = \frac{2S}{2\pi i \rho_1} \left(A - e^{2i\delta} \frac{\omega - i\Delta}{\omega + i\Delta} \right) \quad (\text{II.10})$$

S is the spin of the impurity ($= \frac{1}{2}$ in (II.8)). The amount by which A differs from 1 is a measure for the potential-scattering which is not accounted for by the phase-shift δ , connected with exchange-scattering. We have implicitly assumed that even if $S = 3/2$, only one δ and one Δ are necessary to describe the transport properties. Indeed we have at our disposal only three equations to determine values for A , δ and Δ from experimental results. Using (II.10) one obtains:

$$\text{at } T = 0: \rho = 3.8 S c (A + \cos 2\delta) \quad (\text{II.11a})$$

$$\text{for } T \ll \Delta: d\rho/d(T^2) = -\rho(0) \frac{2 \cos 2\delta}{A + \cos 2\delta} \frac{\pi^2}{3} \frac{c}{\Delta^2} \quad (\text{II.11b})$$

$$,, \quad : \quad S(T) = \frac{k_B}{e} \frac{\sin 2\delta}{A + \cos 2\delta} \frac{2\pi^2 T}{3 \Delta} \quad (\text{II.11c})$$

* This value was obtained assuming that Cu is a free-electron metal. The actual value may be somewhat different, but is difficult to calculate.

Table II.3

fig. II.5	expression (II.10)	Δ (K)	2δ	A	'step' $\mu\Omega$ cm/at.%	pot. scatt. $\mu\Omega$ cm/at.%
I	Nagaoka $S = \frac{1}{2}$	19.7	0	5.07	3.8	7.7
II	all exch. $S = 1.52$	34.3	0	1	11.5	0
III	$S = \frac{1}{2}$	18.8	0.649	5.27	3.0	8.5
IV	$S = \frac{3}{2}$	35.2	0.386	1.097	10.5	1.0

$\rho(0)$ and $d\rho/d(T^2)$ are obtained from table II.2, assuming that $c = 50$ ppm is the correct impurity-concentration. For the thermopower we took $dS(T)/dT = 3 \mu\text{V}/\text{K}^2$ (see chapter III). In table II.3 we have listed some data obtained from various analyses for $T \ll \Delta$. For the first row (Nagaoka) it has been assumed that the temperature-dependent part of the resistivity is described by Nagaoka's expression and that the fraction of the resistivity at $T = 0$, not accounted for by Nagaoka's expression, is caused by potential-scattering. For the second row it has been assumed that all resistivity is due to exchange-scattering, and of the form $\rho = \rho(0) (1 - (\pi^2/3) T^2/\Delta^2)$. The spin-value 1.52 was obtained from (II.11a) with $A = 1$ and $\delta = 0$. In these first two cases the thermopower is zero, thus they are not applicable.

Comparing III and IV we observe only a small amount of potential-scattering for case IV. We have assumed that the resistivity-step (from $T = 0$ to $T \gg T_K$) is approximately given by $3.8 \cos 2\delta \mu\Omega$ cm/at.%. This is only an assumption, but it is approximately correct for the case that potential-scattering has been included in Hamann's theory (see chapter III). Loram et al.⁶⁵ deduced a step-value of about $4 \mu\Omega$ cm/at. % Fe from resistivity-measurements on the (Cu-Au)-Fe system. Thus the value which we obtain in case IV is apparently in disagreement with experiment. To a less extent this is also true for the value of $\Delta \approx T_K$. Loram et al. assume $T_K = 24$ K, which is already high compared to other estimates, which are mostly below 20 K. There is, however, no unambiguous way to determine T_K .

If our description of the Cu-Fe transport-properties at $T \ll \Delta$ by (II.10) is meaningful, then apparently case III of table 3 gives the most reasonable values for the parameters. In fig. II.5 the computed compared to the measured resistivities below 5 K are shown. This picture supports our preference for III. In chapter III we will show that also the thermopower and the Lorenz-number are described reasonably well. The agreement between the computed curve III and experiment looks better than it actually is, however. We neglected any temperature-dependence of Δ (which was predicted by Nagaoka³¹) to be temperature-dependent) and the spin-value of $\frac{1}{2}$ is wrong. This is not necessarily serious, however. The fact that IV does not work merely indicates that we have probably not included the spin in the proper way. We actually represented the scattering by a spin = $\frac{3}{2}$ impurity by three identical scattering mechanisms for spin = $\frac{1}{2}$. We should perhaps take three values of Δ ⁴³) and also three values of δ , but there is no way to determine all these values from experiment, supposed

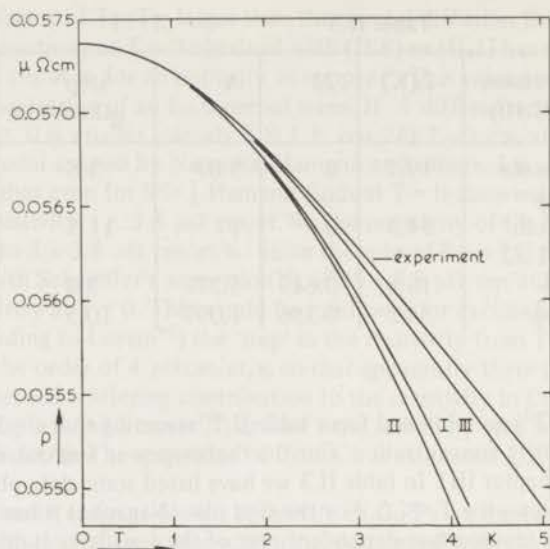


fig. II.5. Measured and computed resistivities of Cu-50 ppm Fe. I, II, III and IV correspond to the same symbols in table II.3 II and IV are nearly equal, only II is shown.

we had introduced them correctly. A clue to this problem may perhaps be provided by the spin-fluctuation theory¹³⁶⁾ according to which at low temperatures the spindensities in all d-orbitals are fluctuating in phase together. This 'acoustic mode' of spinfluctuations might correspond to spin = $\frac{1}{2}$ substituted in (II.10). Spin = $\frac{3}{2}$ might then correspond to independent fluctuations in three orbitals, which case is not realized at low temperatures.

Anyhow, from a phenomenological point of view our description is good and may be useful for comparison of future theories with experiment.

II.6. Interaction effects

In other dilute Cu-Fe alloys we observed a T^2 -term in the resistivity just as in the 50 ppm-specimen discussed in the preceding section. And again we observed a positive deviation from this behaviour at the lowest temperatures, like we have seen in fig. II-4. The most striking example is shown for Cu-30 ppm Fe in fig. II.6. For some reason the positive deviation from the T^2 -line was particularly large in this case, and not consistent with our observations on other Fe-concentrations. The only difference in treatment of the 30 ppm-alloy compared to the others is the 10-hour annealing at 700 °C, after drawing of the wire (see table II.1), whereas the others were not annealed for longer than 4-5 hours. At 700 °C 30 ppm is well below the solubility-limit of Fe in Cu. Nevertheless, we have strong evidence that all deviations from the low-temperature T^2 -dependence are caused by interacting iron-atoms and not by other

magnetic impurities. In particular as regards the magneto-resistance, to be discussed in section II.7, the 30 ppm-alloy behaves very much similar to the other alloys.

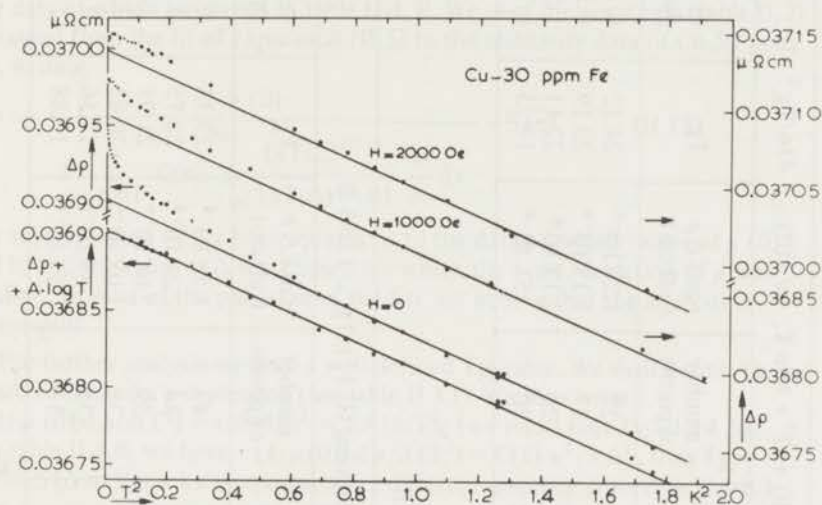


fig. II.6. Impurity-resistivity of a 30 ppm Cu-Fe alloy versus T^2 , below 1.3 K, in magnetic fields $H=0, 1000$ and 2000 Oe. The straight lines have been drawn parallel to each other, consistently with the numerical analysis (see text). A resistivity-maximum in 2000 Oe has only been observed in the 30 ppm-alloy. In the other alloys the $\ln T$ -term was relatively less important; see Table II.4.

In fig. II.6 the lowest series of points shows the actual experimental results minus a term proportional to $\ln T$. Below 1 K the experimental points are very well represented by the straight line. This is particularly striking because below 0.3 K the $\ln T$ -term increases rapidly. In $H=1000$ Oe half of the $\ln T$ -term is suppressed at the lowest temperatures, and in 2000 Oe a resistivity-maximum is observed at about 0.15 K. This maximum is actually the lowest in temperature which has ever been observed. From the $\ln T$ -contribution in $H=0$ we conclude that magnetic particles with a fairly low Kondo-temperature are present. A spin of $3/2$ with a g -factor 2 in a field of 2000 Oe is almost completely saturated at 0.1 K. We do not expect particles with a lower spin-value to be present in our Cu-Fe alloys. In fact, localized magnetic moments of only one Bohr-magneton have never been observed for transition-metal impurities in nonmagnetic metals. We therefore conclude that the particles responsible for the $\ln T$ -term cannot be free moments and probably have a Kondo-temperature of about 0.1 K.

In table II.4 we present the results of an analysis of the resistivity of six Cu-Fe alloys. Data in table II.4.A were obtained by least-squares fitting the resistivity data to the expression $\rho = \rho(0) + a T^2 + b \ln T$. We did not include

Table II.4.A

Analysis of resistivity results using $\rho = \rho(0) + aT^2 + b \ln T$; $-a/\rho(0) = 1.416/T_K^2$

Fe-conc. ppm	$\rho(0)$ $\mu\Omega \text{ cm}$	$-a$ $\mu\Omega \text{ cm/K}^2$	$-b$ $\mu\Omega \text{ cm}$	region (K)	number of points	r.m.s. $\Delta\rho$ ($\mu\Omega \text{ cm}$)	T_K	c_2 ppm	c_2/c^2
30	0.036903	8.98×10^{-5}	1.44×10^{-5}	0.048–0.83	27	1.2×10^{-6}	24.12	0.76	840
50*	0.056972	1.50×10^{-4}	4.47×10^{-6}	0.068–1.0	27	1.1×10^{-6}	23.19	0.23	94
100	0.119403	3.46×10^{-4}	3.00×10^{-5}	0.048–0.89	26	2.1×10^{-6}	22.11	1.58	158
200	0.226597	8.66×10^{-4}	1.28×10^{-4}	0.047–0.62	20	5×10^{-6}	19.25	6.7	168

Table II.4.B

Analysis of the resistivity results using expressing (II.12); $T_K = 1.058 \Delta$

Fe-conc. ppm	$\rho(0)$ $\mu\Omega \text{ cm}$	$\Delta(K)$	$-b$ $\mu\Omega \text{ cm}$	region (K)	number of points	r.m.s. $\Delta\rho$ ($\mu\Omega \text{ cm}$)	T_K	c_2 ppm	c_2/c^2
30	0.036905	22.05	1.36×10^{-5}	0.048–2.1	43	1.5×10^{-6}	23.33	0.71	790
50*	0.056972	21.50	5.11×10^{-6}	0.068–2.0	34	2.2×10^{-6}	22.75	0.27	107
100	0.119401	20.75	3.08×10^{-5}	0.048–2.1	39	2.6×10^{-6}	21.95	1.6	160
200	0.226554	19.50	1.46×10^{-4}	0.047–1.3	32	1.0×10^{-5}	20.63	7.7	190
500	0.60434	16.60	4.45×10^{-4}	0.051–1.3	35	8×10^{-5}	17.56	23	94
460?	0.52774	16.90	2.37×10^{-4}	0.14–1.4	13	5×10^{-5}	17.88	12	59

* The analysis was performed on a different set of measurements on the same specimen as discussed in table II.2.

an analysis of the two most concentrated alloys in table II.4.A, because no non-oscillating fit was possible. This can be understood from the estimated number of magnetic pairs (see below). While determining T_K from these fits (see below), we observed T_K to decrease with increasing Fe-concentration. In order to investigate this effect more carefully we performed another analysis, the data of which are shown in table II.4. B. We used the constants (table II.2) obtained from the fit of expression (II.5) to the resistivity data of Cu-50 ppm Fe, writing:

$$\rho = \frac{\rho(0)}{1 - \sum_{n=1}^6 C(n) \int_{-\infty}^{+\infty} \frac{(xT/\Delta)^{2n}}{(xT/\Delta)^{2n} + 1} \frac{\partial f}{\partial x} dx} + b \ln T \quad (\text{II.12})$$

For various values of Δ a least squares fit to the data provided values of $\rho(0)$ and b , and the value of Δ was chosen for which the r.m.s.-deviation of ρ was smallest. In view of the precision of the fits, we believe that the analysis is meaningful.

For further analysis we need a well-defined T_K -value. We shall define T_K by means of Nagaoka's expression (see table II.3.I). We thus write $-(1/\rho(0))d\rho/d(T^2) = 1.090/\Delta^2 = 1.416/T_K^2$ (we recall that $T_K = 1.14 \Delta$). For table II.4.B. we have $-(1/\rho(0))d\rho/d(T^2) = C(1)\pi^2/3\Delta^2$, thus $T_K = 1.058 \Delta$ (Δ in Nagaoka's expression is a different quantity from Δ in II.4.B.).

Let us now first look at the $\ln T$ -term. From the coefficient of this term we want to determine the concentration c_2 of magnetic particles. In order to do so we could use the expression (I.4) as derived by Kondo. We know however, that Kondo's result is valid only for $\ln T \gg \ln T_K$, and we estimated that in the present case $T_K \approx 0.1$ K, i.e. in the region of measurement. In section I.8 we have seen that Hamann's expression predicts a linear part in the ρ versus $\ln T$ -curve around $T = T_K$, with $d\rho/d \ln T = -2 \hbar c / ne^2 k_F \sqrt{S(S+1)} = -0.602 / \sqrt{S(S+1)} \mu\Omega \text{ cm/at. \%}$.

Objections may be raised against the use of Hamann's result, which is valid only at $T \gtrsim T_K$. Loram et al. obtained a spin-value of 0.77 from a fit of resistivity data on Au-Fe and (Cu-Au)-Fe alloys to Hamann's expression. From magnetic susceptibility we know however that $S \approx 3/2$. If a similar situation occurs in the present case, we are likely to overestimate c_2 , if the correct spin-value were chosen. But probably, the lower T_K the better the s-d exchange model and Hamann's solution of it may describe the actual situation. Besides, the higher the spin-value the wider the temperature-range in which the linear part of the ρ vs. $\ln T$ curve may be observed, and we shall use $S=2.7$. We take this value from Tholence and Tournier¹⁰¹, who obtained it from the analysis of magnetization measurements in Cu-Fe. $S=2.7$ is thus the spin-value of magnetic iron-atom pairs. In table II.4.A and B we see that our estimate of c_2 from the $\ln T$ -term in the low-temperature resistivity is in remarkable agreement with Tholence and Tournier's $c_2 = 130 \text{ c}^2$. The Cu-30 ppm Fe alloy is an exception. It may be that the large $\ln T$ -contribution in this case originates from the 10 hour annealing at 700°C (table II.1).

The agreement between our estimates and those by Tholence and Tournier probably looks better than it actually is, in view of the possible objections against our analysis, which we mentioned above. But the order of magnitude

is likely to be correct. It is possible that magnetic particles are present in Cu-Fe which do show up in the magnetization, but do not show up in the resistivity. This will be the case if T_K of these particles is very low so that the temperature-dependence of the resistivity-contribution is small. Our measurements are not only in agreement with Tholence and Tournier however, but also with Daybell and Steyert's susceptibility measurements⁵¹) and with the specific-heat results of Brock et al.⁹⁷), see section II.7.2., so that we think we are all observing the same kind of interacting Fe-atoms.

We were not able to describe the resistivity of the 460 and 500 ppm alloys by a T^2 and a $\ln T$ -term. This can easily be understood. If we assume $c_2=150 c^2$ (an average over 50, 100 and 200 ppm) then, if $c=500$ ppm, $c_2=38$ ppm. A similar concentration of Fe-atoms in Au will show ordering-effects at 0.1 K (section I.7 : $T_o \approx 20$ K/at.%). So we may not expect the free-spin $\ln T$ -dependence of the resistivity contribution by the 'pairs' in a Cu-500 ppm alloy and the data in table II.4.B for c_2 for both 500 and 460 ppm Fe can only have a qualitative meaning.

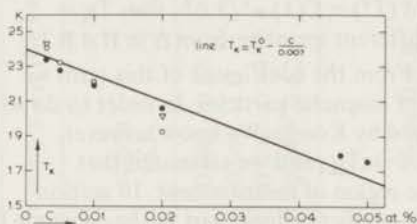


fig. II.7. Kondo-temperature of Cu-Fe versus Fe-concentration.

o: as taken from table II.4.A;

●: as taken from table II.4.B;

▽: see table II.5.

The straight line was drawn with a slope given by $\Delta = \Delta_o - c/2\pi\rho_1$ (II.13). For ρ_1 , the density of states obtained from the electronic specific-heat of Cu was used. $T_K=1.14 \Delta$.

Nominal concentrations were used.

We have implicitly assumed that the magnetic Fe-pairs interact with each other in a similar manner as single Fe or Mn-atoms in Au, or Mn in Cu interact with each other. This assumption is supported by the behaviour of the specific heat (section II.7.2).

The Kondo-temperature of the Cu-Fe alloys can be determined from the T^2 -term in the resistivity, which remains after the $\ln T$ -term has been subtracted. T_K determined in this way appears to decrease with increasing Fe-concentration. In fig. II.7 we plotted the T_K -values from table II.4 versus Fe-concentration. The decrease of T_K is an irrefutable fact (this statement applies only to the region $T \ll T_K$). To a certain extent it depends on the magnitude of the subtracted $\ln T$ -term and the correctness of dividing up the temperature dependence of the resistivity into two terms: $\sim T^2$ and $\sim \ln T$. But the fits shown in table II.4 are very precise for the alloys up to 200 ppm Fe and the magnetoresistance-behaviour (section II.7) is consistent with the analysis. The decrease of T_K is *not* due to deviations from Matthiessen's rule (Appendix I) nor to an error in the subtracted pure-Cu resistivity. If we subtract less for pure Cu the effect is enhanced, in particular for the most dilute alloys, and it is unlikely that we should subtract more.

Stellingen

1. Bij de interpretatie van magnetische ordeningsverschijnselen in verdunde legeringen van palladium en platina met mangaan, ijzer en cobalt dient men rekening te houden met een mogelijke invloed van locale spinfluctuaties.

B. M. Boerstael, proefschrift, Leiden, 1970

2. Nog steeds zijn de 'adopted values' van Keesom de meest betrouwbare gegevens voor de tweede viriaalcoëfficiënt van ^4He boven 4,2 K. Aangezien de $T_{5,8}$ -schaal voor de verzadigde dampspanning van ^4He vermoedelijk systematische fouten bevat en ook de temperatuurschaal boven 4,2 K niet nauwkeurig vastligt, is het gewenst dat p-V isothermen van ^4He beneden 20 K gemeten worden. Ook historisch gezien ligt hier een taak voor het Kamerlingh Onnes Laboratorium.

W. H. Keesom, 'Helium', Elsevier, Amsterdam, 1942, p. 49
J. S. Rogers, R. J. Tainsh, M. S. Anderson en
C. A. Swenson, Metrologia 4(1968)47.

3. Verscheidene auteurs hebben onlangs getracht een positieve term evenredig met T^2 aan te tonen in de elektrische weerstand van verdunde rhodium-ijzer legeringen bij lage temperatuur. Dat zij geen succes hadden, moet er aan worden toegeschreven dat de ijzerconcentratie in hun preparaten minstens een factor tien te hoog was.

B. R. Coles, S. Mozumder en R. Rusby,
Proceedings LT 12, Kyoto, 1970.
N. F. Oliveira Jr. en S. Foner, Phys. Lett. 34A(1970) 15.

4. Uit elektrische weerstandsmetingen aan goud-molybdeen zou men moeten concluderen dat Mo in Au een magnetisch moment heeft. Dit zou uniek zijn voor een overgangsmetaal uit de tweede reeks, opgelost in een ander metaal. Au-Mo verdient daarom opnieuw onderzocht te worden, met zuiverder uitgangsmaterialen zoals die nu beschikbaar zijn.

B. Knook, proefschrift, Leiden, 1962.

5. Uit de röntgenemissie bij beschieting van de vaste stof met ionen leidt men de werkzame doorsnede af voor de productie van röntgenstralen bij ion-atoom botsingen. Bij deze afleiding is ten onrechte de geprojecteerde weg van de ionen in de vaste stof gelijk gesteld aan de werkelijke weg.

E. Merzbacher en H. W. Lewis,
Handbuch der Physik 34(1958) 166.
R. C. Der, R. J. Fortner, T. M. Kavanagh en J. M. Khan,
Phys. Rev. Letters 24(1970) 1272.

6. Het is interessant om experimenteel te onderzoeken of, door voortdurende verlaging van de restweerstand, een ondergrens is vast te stellen voor de coëfficiënt van de T^5 -term, die de elektrische weerstand van een metaal ten gevolge van electron-fonon verstrooiing bij lage temperatuur beschrijft.

Dit proefschrift, fig. I.3.

7. De interpretatie die Chaikin en Jensen geven van hun meetresultaten voor de magnetische susceptibiliteit van verdunde koper-ijzer legeringen is om verschillende redenen aanvechtbaar.

P. M. Chaikin en M. A. Jensen
Solid State Comm. 8 (1970) 977.
Dit proefschrift, Hoofdstuk II.

8. Bij de interpretatie van het gedepolariseerde Rayleigh-spectrum van gassen bestaande uit twee-atomige moleculen wordt door Cooper ten onrechte geen rekening gehouden met een bijdrage in het spectrum, veroorzaakt door de wederzijdse beïnvloeding van de dipoolmomenten der moleculen.

V. G. Cooper, proefschrift, Toronto, 1969.

9. Chouteau en medewerkers vinden een veel lagere waarde voor de Debijetemperatuur van zuiver Palladium dan andere onderzoekers. De door hen gesuggerde verklaring is in tegenspraak met het feit dat hun uitkomst voor de soortelijke warmte der electronen wel in overeenstemming is met door anderen verkregen resultaten.

G. Chouteau, R. Fourneaux, R. Tournier en P. Lederer,
Phys. Rev. Letters 21 (1968) 1082.

10. Terwille van de efficiëntie en de kwaliteit van het verrichte onderzoek dient een wetenschapsbeleid ten aanzien van de natuurkunde het experimenteel en het theoretisch werk zoveel mogelijk te coördineren.

11. Men pleegt op de kleigrond het winterdek op tulpen tot het oogsten te laten liggen, terwijl het op de zandgrond in het voorjaar meestal verwijderd wordt. In het kader van de zuurbestrijding zou men het dek ook op de zandgrond kunnen laten liggen, om aldus te voorkomen dat de grondtemperatuur te hoog woedt.

When we found for the first time indications of a possible concentration-dependence of T_K we observed that the characteristic concentrations at which the effects occurred were in approximate agreement with a calculation by Nagaoka¹⁰). Since then we have purposely searched for such effects.

Nagaoka argued as follows. The conduction-electron states are perturbed by the s-d exchange interaction in an energy-region Δ about the Fermi-energy, i.e. electron-states which play a role in the formation of the 'spin-compensated' state are all within this region. In the case of impurity-spin $\frac{1}{2}$, one conduction-electron spin is needed in the formation of the quasibound state about one impurity (this one spin is collectively supplied, since we are dealing with a many-body effect). We have available $N\Delta\rho_1$ states ($N\rho_1$ is the total electronic density of states per spin) so that not more than $cN = N\Delta\rho_1$ impurities can have a fully developed quasibound state, i.e. we should keep $c < \rho_1 \Delta \approx T_K/T_F$. We encountered this criterion earlier in sections I.9 and II.2.5. According to Nagaoka the expression for the resistivity (I.7) would remain valid for $T \ll \Delta$ and $c \ll \rho_1 \Delta$ with Δ replaced by

$$\Delta = \Delta_0 - \frac{c}{2\pi\rho_1} \quad (\text{II.13})$$

We have compared this prediction with our experimental results for Cu-Fe ($2\rho_1 = 2.5 \times 10^{-5}$ states per Kelvin per electron). The agreement is suspiciously good. Unfortunately, there are no sound reasons to believe in the correctness of Nagaoka's prediction. Although we have shown that a T^2 -term in the resistivity is present, and that a transport relaxation-time of the form given by Nagaoka, if suitably modified, describes also the other transport properties, his calculations were shown to be incorrect⁶²). Furthermore, a long-range negative spin-correlation as predicted by Nagaoka³¹) was not observed, as discussed in section II.2.5. An expression for such a range R of spin-correlations may be obtained if we define a life-time by $\tau = \hbar/\Delta$ and write $R = v_F\tau = \hbar v_F/\Delta$. This range thus is approximately equal to the distance travelled by an electron during the life-time obtained from the width Δ of the quasibound state. If a number of impurities is present such that the electron mean free path $\ell = v_F \hbar \pi \rho_1 / c$ (II.1) is of the same order of magnitude as R we have again $c \approx \pi \rho_1 \Delta$. The criterion obtained in this way is weaker than the criterion obtained if we require that regions of radius R do not overlap, i.e. $c < (T_K/T_F)^3$ instead of $c < T_K/T_F$. The range R has been called coherence-length, like in superconductivity, where a similar characteristic length exists. The analogy with superconductivity is not accidental. Several authors^{31, 109}) have used a theoretical method adapted from superconductivity to treat the magnetic impurity problem. The relation $\Delta = \Delta_0 - c/2\pi\rho_1 = \Delta_0 - \hbar/4\tau_{tr}$. (τ_{tr} is the transport relaxation-time at $\omega=0$) has its counterpart in the relation $T_c = T_c^0 - \pi \hbar/4\tau_s$ for the decrease of the superconducting transition-temperature due to the pair breaking effect of spin-flip scattering by magnetic impurities (τ_s is the time which an electron may travel without having its spin flipped; T_c has been expressed in units of energy).

The critical concentration mentioned above will not necessarily stand or fall with the validity of Nagaoka's calculation. Let us suppose that some type of spin-fluctuation theory described Cu-Fe for $T \ll \Delta$. Let us further assume a

spin-fluctuation life-time $\tau_{sf} \approx \hbar/\Delta^{75}$) and compare it to the transport relaxation-time τ_{tr} . The time τ_{tr} is characteristic for the decay of the electron gas towards equilibrium, after displacement (in *k*-space) by an electric field *E*. The way in which τ_{sf} appears in the resistivity (in the coefficient of a T^2 -term for instance) is probably influenced by the magnitude of τ_{tr} . At low impurity concentrations $\tau_{tr} \gg \tau_{sf}$. By adding more impurities τ_{tr} becomes shorter and if $\tau_{tr} \lesssim \tau_{sf}$ the electron gas, while decaying towards equilibrium, does not 'see' the full decay of a spin-fluctuation, but on the average sees longer lived spin-fluctuations. The characteristic concentration is determined by $\tau_{tr} \approx \tau_{sf}$ i.e. $c \approx \pi \rho_1 \Delta \approx T_K/T_F$. A problem with such an argument is that a number of characteristic times may be of importance. In addition to a life-time of spin-fluctuations one has a life-time of charge-fluctuations, associated with the virtual bound state in Friedel's sense. Heeger proposed¹³) a third characteristic time, associated with the spin correlations in the Kondo-effect. The relative magnitude of all these characteristic times depends on the electronic structure of the impurity in the metal and the assumption $\tau_{sf} \approx \hbar/\Delta$ is not necessarily correct for Cu-Fe, with Δ determined from experiment in the way we did.

If we had observed a decrease of the apparent T_K -value with increasing impurity-concentration in Cu-Fe only, we would not have paid much attention to the effect. But in Pd-Cr and Pt-Cr we observed a similar phenomenon (Chapter IV) without a low-temperature logarithmic deviation from the T^2 -behaviour and we think that the interpretation is important to the understanding of magnetic impurities in metals.

The interaction-effect as predicted by Nagaoka¹¹⁰) and discussed above in connection with fig. II.7, is not the only possible interpretation of the experimental results. The agreement between Nagaoka's prediction and our experimental results may even be purely accidental. The interactions at relatively short distances, responsible for the 'magnetic pairs' caused T_K to decrease from about 20 K to about 0.1 K. At greater distances the same type of interaction will be weaker and may cause a less drastic decrease of T_K for a number of iron impurities. So in fact a wide range of Kondo-temperatures may occur, corresponding to various impurity interaction-strengths. Let us assume that at $T=0$ Cu-Fe is non-magnetic in the Friedel-Anderson sense. Spatial oscillations of charge-density will occur about the virtual state¹²³). Anderson's criterion for impurity magnetism⁴⁶) depends on the local density of states. The charge oscillations may cause impurities to move away from or towards and across the boundary for magnetism, depending on the presence and distance of neighbouring impurities. Such effects have been suggested by Caroli¹²⁴). Recently Kim¹²⁵) published a calculation of local environment effects on the basis of Anderson's model for more than one impurity. The theory gives only qualitative results, but confirms the possibility of various suggestions which have been put forward to interpret experimental results. Thus isolated V-atoms in Au may be magnetic whereas nearest neighbour pairs are nonmagnetic (see also section II.8). The reverse situation may occur for Co in Au. In fact, from an analysis of magnetization results Boucaï et al.¹²⁶) proposed $T_K=190$ K for isolated Co-atoms in Au and $T_K=23$ K for pairs. Groups of three or more neighbour-atoms are magnetic (i.e. $T_K < 1$ K). There is one important difference however between alloys like Cu-Co and Au-Co on one

hand and Cu-Fe, Pd-Cr and Pt-Cr on the other, namely that a T^2 -term in the low-temperature resistivity has been observed in the latter alloys. Such a temperature-dependence has not been observed in Cu-Co, and Au-Co, not even for very low Co-concentration¹²⁷). It is not yet clear whether this difference is only gradual, or whether the apparent local environment-effect is enhanced by solubility problems in Au-Co or Cu-Co. The magnetic moment in Au-Co anyhow appears discontinuously, i.e. pairs are weakly magnetic and groups of more atoms are magnetic. In Pt-Cr and Pd-Cr changes in the magnetic state of Cr appear continuously with increasing concentration. In a certain sense this is also the case for Cu-Fe. It is quite remarkable that only two parameters ($\ln T$, T^2) are necessary to describe the temperature-dependence of the Cu-Fe resistivity at low temperatures and low concentrations, although the interactions are fairly long-range. If we take $c_2 = 150 c^2$ and assume, following Tholence and Tournier¹⁰¹) that the charge oscillations about Fe produce both magnetic and non magnetic pairs (the latter will have $T_K \gg 20$ K and cannot be observed), then about $600 c^2$ Fe-atoms in the dilute alloy are coupled to a neighbour. It follows that the range of interaction covers 600 Cu-sites about each Fe-centre, i.e. 12 \AA . We think it is surprising that Fe-atoms within 12 \AA from each other interact to become nonmagnetic or magnetic with $T_K \approx 0.1$ K, whereas Fe-atoms without neighbours in that range have a $T_K \approx 20$ K. This is actually the case, otherwise our analysis (table II.4) would not have been possible. We therefore suggest that the $\ln T$ -term in the resistivity may not be of purely statistical origin, although the approximate c^2 -dependence is an indication of the contrary. In Cu-Fe too, the number of magnetic particles may be enhanced by the poor solid solubility of Fe in Cu. We also think that the possibility, that the low-temperature concentration-dependence of T_K as predicted by Nagaoka actually occurs, cannot be entirely ruled out.

II.7. Comparison with other experiments

II.7.1. Magnetoresistance and magnetic susceptibility

In this subsection we present an analysis of the low-temperature magnetoresistance of three Cu-Fe alloys. From the analysis we want to obtain an estimate of the magnetic field-dependence of the susceptibility.

The maximum external field was 2000 Oe, so that $H \ll H_K$ (section II.5) and we do not expect an effect on the resistivity contribution by isolated Fe-atoms. We will thus neglect the magnetoresistance of isolated Fe-atoms in Cu. The $\ln T$ -term however is strongly suppressed in a magnetic field, as was shown already in fig. II.6. In order to perform the analysis it would be very convenient to have the disposal of a function which describes the temperature and magnetic field-dependence of the magnetoresistance. Béal-Monod and Weiner¹²⁸) have shown that at $T \gg T_K$ and $\mu_{\text{eff}} H < 2 k_B T$ the magnetoresistance $\Delta\rho_H$ is proportional to M^2 (M is the magnetization). At $1 \text{ K} < T < T_K$ these authors analysed the magnetoresistance of Cu-Fe assuming that also below T_K the relation $\Delta\rho_H \sim M^2$ might hold. The results obtained from the analysis were not unreasonable. In our analysis we shall therefore

Table II.5

Analysis of the Cu-Fe magnetoresistance using $\rho = \rho(0) + aT^2 + b \ln T + dB_{0.2}^2$ (II.14)								
Fe-conc. ppm	H Oe	$\rho(0)$ $\mu\Omega \text{ cm}$	a $\mu\Omega \text{ cm/K}^2$	b $\mu\Omega \text{ cm}$	d $\mu\Omega \text{ cm}$	d/b	region (K)	r.m.s. $\Delta\rho$ $\mu\Omega \text{ cm}$
30	0	0.036902	-8.85×10^{-5}	-1.48×10^{-5}	—	—	0.048–1.13	1.5×10^{-6}
	1000	0.036967	—	—	-3.66×10^{-5}	2.47	0.053–1.14	1.6×10^{-6}
	2000	0.037139	—	—	-3.72×10^{-5}	2.51	0.053–1.14	1.6×10^{-6}
100	0	0.119403	-3.46×10^{-4}	-3.00×10^{-5}	—	—	0.048–0.89	2.1×10^{-6}
	1000	0.119424	—	—	-6.19×10^{-5}	2.06	0.050–0.85	3.0×10^{-6}
	2000	0.119498	—	—	-6.41×10^{-5}	2.14	0.067–0.90	3.3×10^{-6}
200	0	0.226576	-7.87×10^{-4}	-1.36×10^{-4}	—	—	0.048–0.82	7×10^{-6}
	1000	0.226582	—	—	-2.52×10^{-4}	1.85	0.056–0.82	8×10^{-6}
	2000	0.226586	—	—	-2.51×10^{-4}	1.85	0.065–0.82	1.2×10^{-5}

Temperature regions for 30 and 200 ppm differ from table II.4.A. Values of T_K and c_2 also differ slightly. For 30 ppm $T_K = 24.30$, $c_2 = 0.78$ ppm; for 200 ppm $T_K = 20.19$, $c_2 = 7.1$ ppm; T_K values have been indicated in fig. II.7.

assume that $\Delta\rho_H \sim M^2$, at all H and T and that M is a function of H/T. Furthermore, we shall assume that M is proportional to a Brillouin-function. This assumption is purely phenomenological. In fact it turned out that $J=0.2$ was the best choice for the Brillouin-function, which is not very much consistent with $S=2.7$. We might have used any other suitable function of H/T.

A least squares fit of the resistivity data to the expression

$$\rho = \rho(0) + aT^2 + b \ln T + d B_{0.2}^2 \quad (\text{II.14})$$

was made. At $H=0$, $B_{0.2}=0$ and $\rho(0)$, a and b were determined.

These values of a and b were used to determine $\rho(0)$ and d at $H=1000$ and 2000 Oe. We notice that $\rho(0)$ depends on H because of the positive magnetoresistance of pure Cu.

In table II.5 we give the results of the analysis of the magnetoresistance for three Cu-Fe alloys. The Cu-50 ppm Fe alloy was not analysed because of the smallness of the $\ln T$ -term. For Fe-concentrations above 200 ppm the analysis is not possible because a well defined $\ln T$ -term was not observed (section II.6).

It may be noticed that the fits are fairly precise. The values of d, obtained for the two fields for each alloy, are nearly the same. Furthermore d/b does not change very much with Fe-concentrations. This convinces us that the type of impurity, responsible for the $\ln T$ -term, is the same in all three alloys and that our way of analysis is meaningful. We think it is remarkable that d/b changes so little, while c_2 differs by a factor of 10 between 30 and 200 ppm Fe (see table II.5). There is clearly *no wide spectrum of Kondo-temperatures* like suggested by Souletie¹²⁹. It is well known that the absolute positive magnetoresistance in dilute (nonmagnetic) alloys decreases with increasing impurity concentration. This is also observed in $\rho(0)$ of table II.5. For the 200 ppm alloy $\rho(0)$ is nearly independent of magnetic field.

The way in which our analysis works out is shown again in fig. II.8. We choose Cu-30 ppm Fe because the $\ln T$ -term is relatively most important in this alloy. In $H=2000$ Oe below 0.06 K the computed curve begins to increase again with decreasing temperature. The Brillouin-function is nearly saturated but $\Delta\rho_H$ is not, because of the increasing $\ln T$ -term. In fact, even if $B_{0.2}$ would correctly describe the magnetization, one may not expect $\Delta\rho_H \sim M^2$ if M is nearly saturated¹²⁸.

We venture one physical conclusion from the fact that $B_{0.2}$ was best suited for our analysis of the magnetoresistance. Since $S=2.7$ was obtained from magnetization measurements above 1.3 K¹⁰¹) the magnetic pairs are certainly not free-spin moments below 1 K. We estimated $T_K \approx 0.1$ K for the pairs (section II.6). This estimate is in good agreement with the early susceptibility measurements by Daybell and Steyert³⁷), represented as $\chi = (2.52/(T+14) + 0.168/(T+0.045)) \times 10^{-8}$ e.m.u./g ppm Fe, if we recall that the Curie-Weiss temperature is generally of the order of T_K .

If we had at our disposal a theoretical expression for the magnetization at

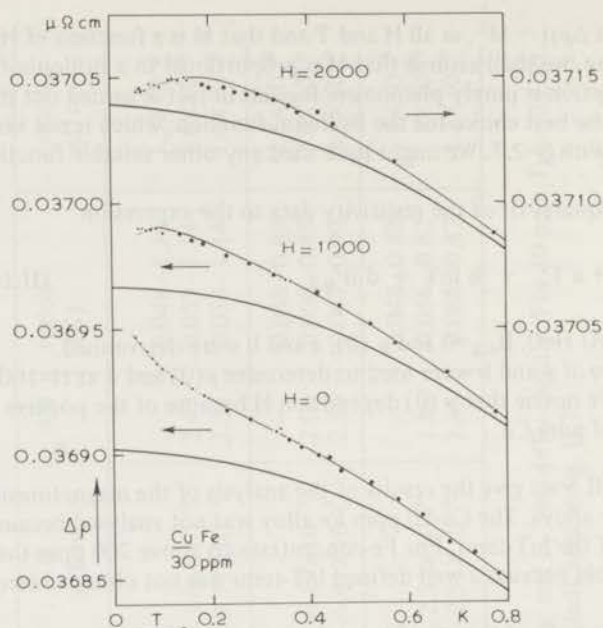


fig. 11.8. Analysis of the magneto-resistance of Cu-30 ppm Fe. The three parabola's represent $\rho = \rho(0) - 8.85 \times 10^{-5} T^2 \mu\Omega \text{ cm}$, where for each field the appropriate value of $\rho(0)$ was substituted. The curves drawn through the points represent the computed fits to expression (11.14).

$T \approx T_K$ we could draw some conclusions from the value of d/b . Such an expression has never been calculated for that temperature region however. We shall nevertheless try to relate the magneto-resistance to the field-dependence of the susceptibility. We notice that it is not possible to distinguish unambiguously

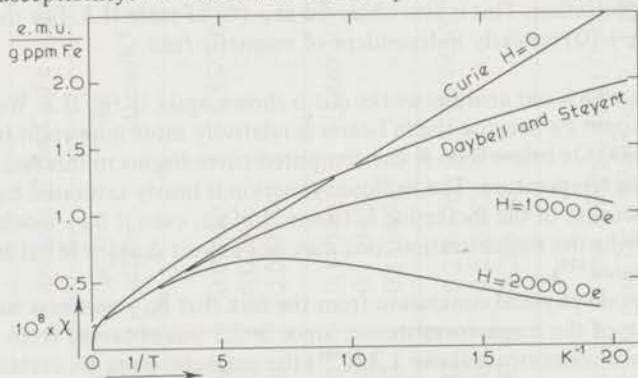


fig. 11.9. Susceptibility of Cu-100 ppm Fe as estimated from the magneto-resistance. In $H=0$: $\chi = (0.17 + 0.12/T) \times 10^{-8} \text{ e.m.u./g ppm Fe}$. The constant accounts for the isolated Fe-atoms: $\mu^2 \text{ eff}/3 k_B \theta = 0.17 \times 10^{-8} \text{ e.m.u./g ppm Fe}$ with $\mu \text{ eff} = 3.68 \mu_B$ and $\theta = 16 \text{ K}$ according to Daybell and Steyert⁵¹⁾
 In 1000 and 2000 Oe: $M = 2.2 \times 10^3 B_{0.2} \text{ e.m.u./g ppm Fe}$: $\chi = \partial M/\partial H$. The curve of Daybell and Steyert represents Cu-110 ppm Fe³⁷⁾.

between $\Delta \chi \sim T^{-1}$, $\sim T^{-1/2}$ or $\sim 1/(T + 0.045)$ from Daybell and Steyert's susceptibility data^{37,51}). Let us assume $c_2 = 150 c^2$ and express the low-field susceptibility by a Curie-law $\chi = c_2 g^2 S(S+1) \mu^2 B / k_B T$. With $g=2$ and $S=2.7$ we have $\chi = 0.12 \times 10^{-8} / T$ e.m.u./g ppm Fe for Cu-100 ppm Fe. This is shown in figure II.9. There is clearly no great difference between the estimate and Daybell and Steyert's measurement.

In order to estimate the magnetic field-dependence of χ we assume that $M \sim B_{0.2}$ in view of the analysis of the magnetoresistance. We shall *not* compute M as if the magnetic pairs were free moments with $S=0.2$. Instead, as remarked before, $B_{0.2}$ is used only as a phenomenological description of $M(H/T)$. So, as $B_{0.2} = 5.37 \times 10^{-5} H/T$ e.m.u. ($\mu H \ll kT$) and $M = 0.12 \times 10^{-8} H/T$ e.m.u./g ppm Fe, we write $M = 2.2 \times 10^3 B_{0.2}(H/T)$ e.m.u./g ppm Fe for Cu-100 ppm Fe. This is shown for $H=0, 1000$ and 2000 Oe in fig. II.9.

Taking into account the weaknesses in our assumptions there is good agreement between our estimate and Daybell and Steyert's measurement of the susceptibility, in zero field as well as in $H=1000$ and 2000 Oe. (ref. 51 : fig. 2). In Daybell and Steyert's work the $T^{-1/2}$ -term seems to be suppressed already above 1000 Oe, but this cannot be decided unambiguously owing to the scatter of their experimental points.

Tholence and Tournier remark that the Curie-law susceptibility obtained using $c_2 = 130 c^2$ and $S=2.7$ is on the average a factor of six larger than would follow from a representation of Daybell and Steyert's results⁵¹), by a Curie-law. They assume that one sixth of all pairs is magnetic (free-spin moment) and that the rest of the pairs is nearly magnetic with T_K of order 1 K. The magnetization measurements above 1 K cannot distinguish between these two types of pairs. This assumption would be in agreement with the work of Golibersuch and Heeger¹⁰⁰) who suppose that 1% of the Fe-atoms in Cu-460 ppm Fe is precipitated in the form of single-domain ferromagnetism particles, in order to explain the magnetic field-dependence of the Cu⁶³ N.M.R. linewidth at 1.2 K. Indeed 1% of 460 ppm is equal to $1/6 \times 130 c^2$. The anomalous low-field contribution to the linewidth is, however, not necessarily saturated above 3000 Oe, as assumed by Golibersuch and Heeger. The linewidth versus external field plot is not a straight line above 3000 Oe (ref. 100, figs. 19, 20) and the remaining curvature may have the same origin as the initial curvature. The extrapolation of a straight line towards $H=0$ depends on which part of the linewidth vs. external field curve is chosen to be a straight line. Furthermore we remarked already in section II.2.5 that the residual linewidth at very low temperatures of a Cu-410 ppm Fe alloy¹⁰²) is accounted for by the presence of about 25 ppm particles with spin ≈ 3 , saturated in the external magnetic field, in agreement with $c_2 \approx 150 c^2$. We believe therefore that it is not necessary to make the distinction between magnetic and nearly magnetic pairs, like Tholence and Tournier do. This is also true for the susceptibility results of Daybell and Steyert. For 50 ppm Fe the experimental results are only a factor 2 (not 6) smaller than the estimate on the basis of a Curie-law, $c_2 = 150 c^2$ and $S=2.7$. Furthermore the $T^{-1/2}$ -contribution of Daybell and Steyert increase more rapidly than $\sim c$, but slower than $\sim c^2$ between 54 and 330 ppm Fe. Moreover, their first susceptibility result³⁷) is in agreement with our estimate (fig. II.8). In view of the importance of the thermal history to the properties of Cu-Fe

(table II.1, ref. 101) and possible errors in the Fe-concentration, we can safely assert that the same kind of magnetic iron particles (pairs) is responsible for the observed low-field effects in the magnetic susceptibility^{37,51}, Cu⁶³ linewidth¹⁹², magnetization¹⁰¹, resistivity, and specific heat (section II.7.2).

Having accounted for the susceptibility-anomaly one may ask what is the susceptibility of non-interacting Fe-atoms. Up till now most analyses of susceptibility-measurements have been performed by means of fitting the data to a Curie-Weiss type expression. Below T_K the physics behind such an analysis is unclear however. In view of the fact that $\Delta\rho \sim -T^2$, $\Delta C \sim T$ (section II.7.2.) and in view of the achievements of spin-fluctuation-theories⁷³) it is likely that the susceptibility is finite at $T=0$, of the order of $\mu^2_{\text{eff}}/3 k_B T_K$ and decreases proportionally to T^2 with increasing temperature from $T=0$. It would be of conceptual importance to observe such a temperature-dependence but experimentally this will be extremely difficult.

II.7.2. Electrical resistivity and specific heat

In section II.2.2 we have briefly reviewed the history of specific-heat measurements on Cu-Fe. In this section we shall compare our resistivity results with the specific heat measurements by Brock et al.⁹⁷, and by Franck et al.⁹⁵) to show the similarity in concentration-dependence and to support the idea that for $c \lesssim 100$ ppm Fe the specific heat contribution of Fe in Cu is proportional to T .

In fig. II.10 the electrical resistivity is shown for five dilute Cu-Fe alloys, normalized to 100 ppm Fe at 2.14 K. The small $\ln T$ -anomaly discussed in

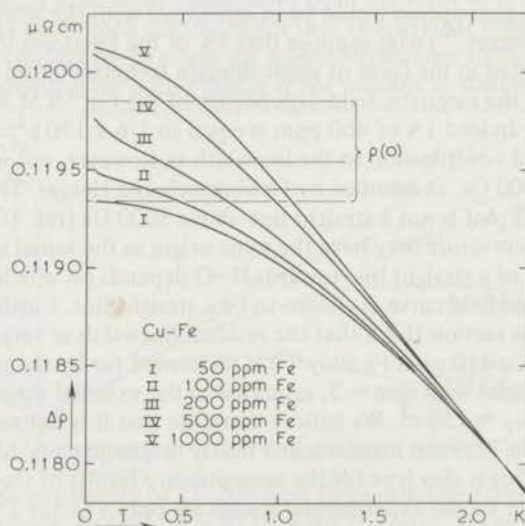


fig. II.10. Electrical resistivity of five Cu-Fe alloys, normalized to 100 ppm at 2.14 K; for the lowest four concentrations $\rho(0)$ of table II.4 has been indicated by horizontal bars.

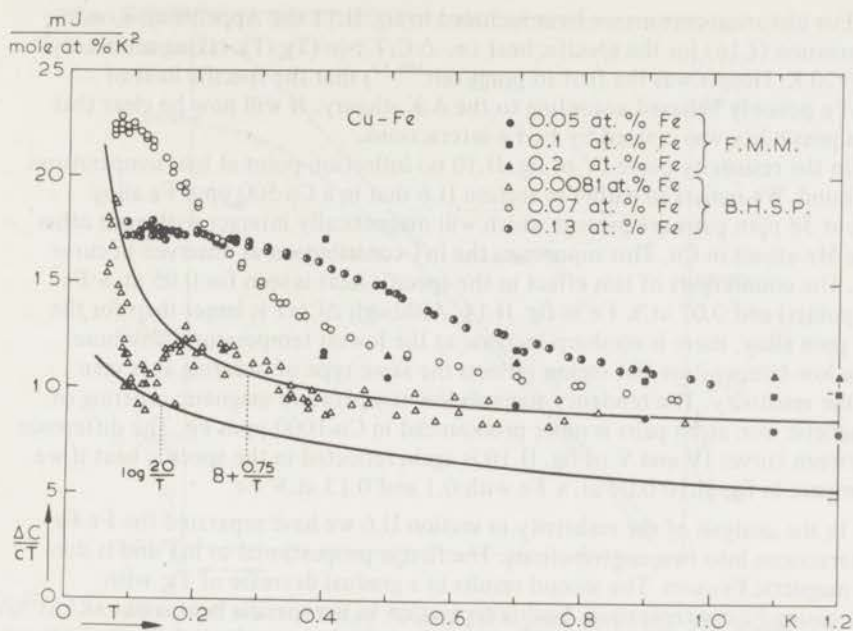


fig. 11.11. Specific heat data for Cu-Fe, taken from Franck, Manchester and Martin (F.M.M.)⁹⁵ and from Brock, Ho, Schwartz and Phillips (B.H.S.P.)⁹⁷. The curves are explained in the text.

section II.6 was subtracted for Cu-50 ppm Fe (it would have been almost invisible in fig. II. 10). In curves II and III one observes an inflection point at about 0.2 K, caused by the increasing $\ln T$ -term. The equivalent of this $\ln T$ -term in the temperature dependence of the specific heat can be observed in fig. II.11. $\Delta C/cT$ for the lowest concentration (81 ppm Fe) apparently increases with decreasing temperature. The large scatter of the points reflects the difficulty of performing precise measurements of small specific heats at such low temperatures. There is considerably less scatter for the higher concentrations. Nevertheless we believe that the sharp increase of $\Delta C/cT$ below 0.1 K is real. We can actually account for it. We assume as before that the magnetic iron pairs have $T_K \approx 0.1$ K. We notice that the specific-heat contribution by magnetic impurities due to the Kondo-effect has a broad maximum around T_K . For Cu-Fe ($S \approx 3/2$) the specific-heat value at the maximum is 30 mJ/mole K at.% Fe. We shall arbitrarily assume that for the pairs ($S \approx 2.7$) the specific-heat maximum has a value of 60 mJ/mole K at.% Fe-pairs around 0.1 K. This is certainly an overestimate. With $c_2 = 150 c^2$ and $c=81$ ppm we have 1 ppm pairs with a specific-heat contribution of 0.75 mJ/mole K at.% Fe. We take the specific heat-contribution by isolated Fe-atoms to be proportional to T , and the pair-contribution constant i.e. $\Delta C/cT = 8 + 0.75/T$ mJ/mole at.% Fe K^2 . The curve representing this expression has been drawn in fig. II.11. The agreement with the experimental points is very good, and would be even better if we had used a smaller (less overestimated) value for the contribution per pair.

For historical reasons we have included in fig. II.11 the Appelbaum-Kondo expression (I.16) for the specific heat i.e. $\Delta C/T \sim \ln(T_K/T)$, taking arbitrarily $T_K=20$ K. Heeger was the first to point out^{102,13)} that the specific heat of Cu-Fe possibly behaved according to the A.K.-theory. It will now be clear that this possibility was created by Fe-Fe interactions.

In the resistivity-curve IV of fig. II.10 no inflection-point at low temperatures is found. We remarked earlier in section II.6 that in a Cu-500 ppm Fe alloy about 38 ppm pairs are present which will magnetically interact with each other like Mn-atoms in Cu. This suppresses the $\ln T$ -contribution as observed in curve IV. The counterpart of this effect in the specific heat is seen for 0.05 at.% Fe (6 points) and 0.07 at.% Fe in fig. II.11. Although $\Delta C/cT$ is larger than for the 81 ppm alloy, there is no sharp increase at the lowest temperatures anymore. The low-temperature flat region reflects the same type of ordering as is seen in the resistivity. The tendency towards low-temperature magnetic ordering of magnetic iron atom pairs is more pronounced in Cu-1000 ppm Fe. The difference between curves IV and V of fig. II.10 is again reflected in the specific heat if we compare in fig. II.10 0.07 at.% Fe with 0.1 and 0.13 at.% Fe.

In the analysis of the resistivity in section II.6 we have separated the Fe-Fe interactions into two contributions. The first is proportional to $\ln T$ and is due to magnetic Fe-pairs. The second results in a gradual decrease of T_K with increasing Fe-concentration. Such a separation in the specific heat is not as straightforward, because of the limited precision of the results and the limited number of concentrations studied below 0.05 at.%. From the electrical resistivity we estimate a decrease of T_K with 25% from 100 to 500 ppm Fe (fig. II.7). Qualitatively such a decrease may be observed in fig. II.11, if we assume that $\Delta C \sim T/T_K$, but the pair-contribution is probably of the same magnitude. The amount of entropy exhibited per at.% Fe below 1 K increases with concentration up to 0.1 % Fe. This is made up for above 4 K. In the results of Franck et al.⁹⁵⁾ the specific heat per at.% Fe in Cu above 4 K is largest for the lowest Fe-concentration. In order to emphasize in this context how important interaction effects are in Cu-1000 ppm Fe, also above 1 K, we compare the resistivities of 50 and 1000 ppm Fe in Cu up to 4 K (fig. II.12). In addition to the effects noticed already in fig. II.11., one observes that at 4 K $d^2\rho/dT^2 < 0$ for 50 ppm (inflection point at $T \approx 5$ K) whereas $d^2\rho/dT^2 > 0$ for 1000 ppm (the difference is small but real). Evidently in Cu-1000 ppm Fe the pair-contribution to the resistivity together with the apparent decrease of T_K have caused the inflection-point of the resistivity-curve to shift more than 1 K towards lower temperatures. It is interesting to notice the striking qualitative similarity between fig. II.12 and fig. 6 of the paper by Nagaoka¹¹⁰⁾ dealing with interaction effects. We have repeatedly emphasized that Nagaoka's results and ideas are not necessarily correct. But they provide a very convenient framework for the discussion of our experimental results. Besides there is only one alternative, namely a spin-fluctuation theory, which has not yet been worked out satisfactorily for application to an alloy like Cu-Fe.

Using Nagaoka's expression for the specific heat¹³⁰⁾

$$C = \frac{2\pi}{3} \frac{T}{\Delta} \quad (\text{I.17})$$

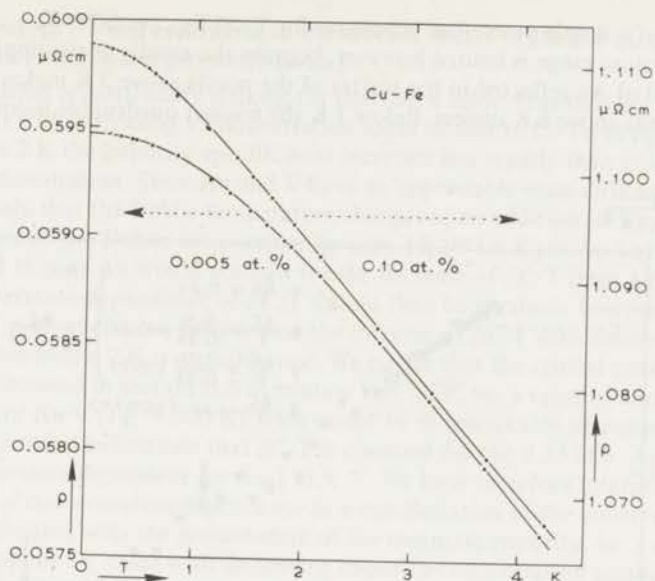


fig. II.12 Electrical resistivities of 50 and 1000 ppm Fe in Cu. The scales are in proportion to the resistivity values, so that the picture is qualitatively similar to fig. II.10.

per impurity, one can evaluate Δ . With $C/cT = 8 \text{ mJ/mole K}^2$ at.% Fe one finds $\Delta = 22 \text{ K}$, thus $T_K = 25 \text{ K}$ ($T_K = 1.14 \Delta$). This value agrees well with T_K obtained from resistivity measurements (section II.5).

II.8. Some remarks on Gold-Vanadium

Quite soon after Cu-Fe, Au-V was proposed⁵⁴) as a system with a 'high' Kondo temperature, namely $T_K \approx 300 \text{ K}$. We have included this system in our investigations of physical properties below T_K . Our investigation of Au-V was not as extensive as of Cu-Fe however, for reasons which will become clear below.

II.8.1. Specific heat

Due to the high Kondo-temperature, the specific-heat contribution per V-atom in Au is rather small. Furthermore the Debye-temperature of Au is relatively low (162 K) so that the specific heat of the host increases rapidly with temperature. This is a serious drawback to the precise experimental determination of the temperature-dependence of the Vanadium-contribution to the specific heat. In fig. II.13 the impurity contribution of the specific heat of three dilute Au-V alloys is shown *) The behaviour of the most dilute alloy supports our

*) The measurements have been performed by B.M. Boerstael and coworkers. Experimental details may be found in refs. [131] and [132].

conjecture of a simple power-law behaviour for $T \ll T_K$, i.e. $\Delta C \sim T$. The temperature range is limited however, because the rapidly increasing lattice specific-heat of Au reflected in the scatter of the points above 3 K makes measurements above 6 K useless. Below 1 K the nuclear quadrupole moments

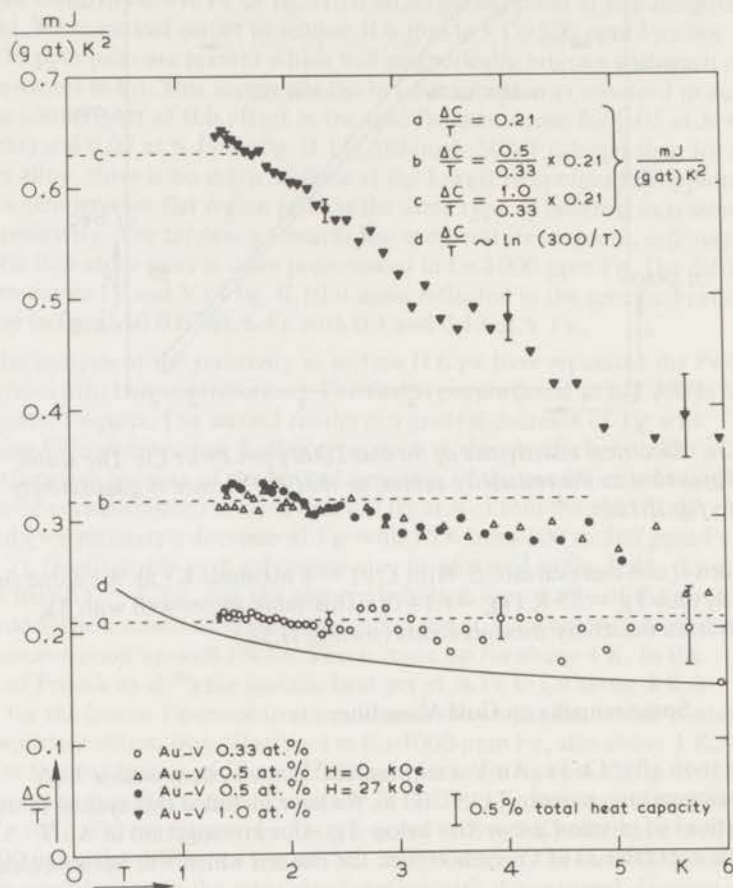


fig. 11.13 Impurity contribution to the specific heat of dilute Au-V alloys. Dashed lines show the values of $\Delta C/T$ for (assumed) concentration-independent behaviour. The full line represents the Appelbaum-Kondo expression normalized to the specific heat of the 0.33 at. % alloy at 1 K. It should be noted that for comparison of this expression with the 0.5 at. % alloy the curve d should be multiplied by $0.5/0.33$ and then also deviates from the experimental data. As we expect with $T_K = 300$ K a magnetic field of 27 kOe has no measurable effect on the specific heat (0.5 at. % V). Alloys were prepared by induction melting under Argon atmosphere in Al_2O_3 crucibles. They were homogenized during 48 hours in vacuum at $1000^\circ C$ and subsequently quenched in water. Vanadium concentrations are accurate to within 5%.

of V^{51} and Au^{197} will contribute to the specific heat. For the 0.5 at. % and 1 at. % alloys ΔC is not proportional to T .

The deviation is particularly striking for the 1 at. % alloy. Qualitatively the behaviour with increasing V-concentration looks similar to Cu-Fe in fig. II.11, but above 2 K the impurity specific-heat increases less rapidly than proportional to the concentration. Since Au and V have an appreciable mass difference it is not unlikely that the Debye-temperature changes upon addition of Vanadium. An increase of the Debye-temperature by only 1% (= 1.6 K) in Au-1 at. % V as compared to pure Au would account for the decrease of $\Delta C/T$ from 1 to 6 K. The temperature-dependence of $\Delta C/T$ should then be parabolic however. This is not the case, so that we believe that the increase of $\Delta C/T$ with decreasing temperature below 2 K is probably real. We notice that the critical concentration T_K/T_F , discussed in section II.6 in relation to Cu-Fe, has a value of about 0.5 at. % for Au-V ($T_K \approx 300$ K). This would be in remarkable agreement with the experimental indications that $\Delta C/T$ is constant for the 0.33 at. % Au-V alloy and temperature-dependent for Au-1 at. % V. We have therefore interpreted¹³³⁾ this type of concentration-dependence as a manifestation of the coherence-length associated with the ground-state of the magnetic impurity, i.e. a decrease of the apparent T_K -value with decreasing impurity-concentration according to Nagaoka (section II.6). However, the negative spinpolarization of a range equal to the coherence-length was not observed in Cu-Fe¹¹²⁾ nor in Au-V¹³⁴⁾, so that one may question if a coherence-length actually exists. We will devote some more discussion to interaction-effects in Au-V in the next subsection, with regard to the resistivity.

In fig. II.13 we have included a plot of the Appelbaum-Kondo expression (I.16) to show it is not easy to distinguish experimentally between several possibilities if there are no sound theoretical arguments to prefer one to the others. In the present case the A.K.-expression can be left out of consideration and $\Delta C \sim T$ is most appropriate, in particular if one agrees with Narath¹¹³⁾ that V in Au at low temperatures is simply nonmagnetic in the Friedel-Anderson sense.

To be consistent with our earlier analysis let us determine T_K for Au-V by means of Nagaoka's expression (I.17). Using $\Delta C/T=0.21$ mJ/mole K^2 for Au-0.33 at. % V we find $T_K=310$ K, in good agreement with other estimates⁵⁴⁾.

II.8.2 Electrical resistivity

We have not succeeded in unambiguously demonstrating the presence of a T^2 -term in the electrical resistivity of dilute Au-V alloys below 4 K. Heeger¹³⁾ includes a picture of resistivity results on Au-V by Loram et al., fitted to the Appelbaum-Kondo expression (I.15) with $T_K=300$ K, from 0.5 – 12 K. This looks satisfactory, but application of our criterion $c < T_K/T_F \approx 0.5$ at. % shows that interaction effects are likely to occur, since the concentrations of Loram et al. were 0.8 at. % and 2 at. % V. Indeed, inspection of the curves (fig. 29 of ref.¹³⁾) shows that $\rho(1\text{ K})/\rho(4\text{ K})=1.00034$ for Au-0.8 at. % V and $\rho(1\text{ K})/\rho(4\text{ K})=1.00048$ for Au-2 at. % V. If the residual resistivity is proportional to the V-concentration this means that $|d\rho/dT|$ increases more rapidly than proportional to the concentration. There is a remarkable similarity

between this effect and the concentration-dependence of the Cu-Fe resistivity, as shown in fig. II.10 and pointed out by us⁸⁴) in an earlier publication.

Clearly, if we want to observe the contribution of non-interacting V-atoms to the resistivity in Au-V we must keep the concentration below 0.5 at. % V. The temperature-dependence of the V-contribution to the resistivity is very small however and very small amounts of Fe-contamination are likely to be present in pure Au, hampering the determination of this V-contribution. We have prepared several dilute Au-V alloys using very pure gold (Cominco 6 N) and Vanadium (zone refined). We always found ρ versus T^2 to be curved. In fig. II.14 we show

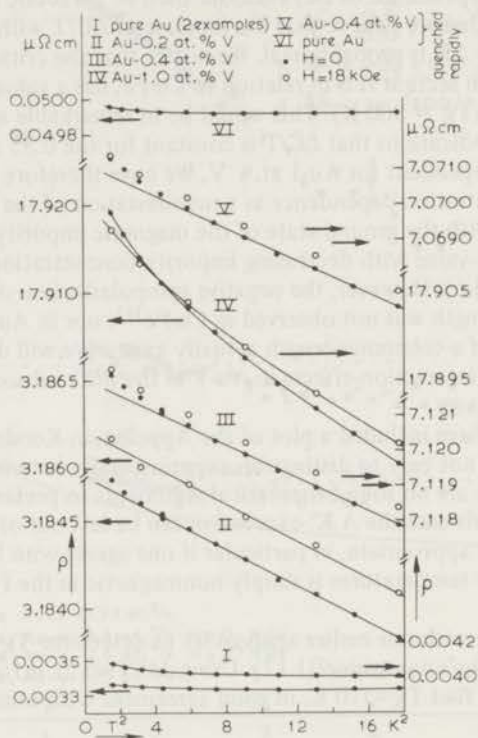


fig. II.14. Electrical resistivity of some dilute Au-V alloys. All alloys were prepared by induction melting under an Argon atmosphere. I, II, III and IV were homogenized in vacuum during 24 hours at 1000 °C, quenched in water and drawn to wires. Only I was annealed after drawing (3,5 hours at 600 °C). V and VI were rapidly quenched by letting liquid droplets fall into water. Both were drawn into wires but not annealed. Rapid quenching apparently made no difference to the temperature-dependence of the resistivity. Neither did annealing at 600 °C of I – III after drawing of the wires (results not shown). Straight lines were drawn to show the deviations from $\Delta\rho \sim T^2$ for II, III and V. Notice that for the alloys the resistivity of pure gold has not been subtracted. For $H=0$ we observed:

$$\begin{array}{ll}
 \text{II: } \rho(1\text{ K}) / \bar{\rho}(4\text{ K}) = 1.00026 & \text{V: } \rho(1\text{ K}) / \rho(4\text{ K}) = 1.00055 \\
 \text{III: } \rho(1\text{ K}) / \rho(4\text{ K}) = 1.00055 & \text{IV: } \rho(1\text{ K}) / \rho(4\text{ K}) = 1.00156
 \end{array}$$

some examples. The resistivity-curves of the pure gold specimens demonstrate that deviations from $\Delta\rho \sim T^2$ are probably not caused by impurities introduced during the preparation. Only for II the points do not significantly deviate from the straight line. Applying as before Nagaoka's expression (I.7), with $d\rho/dT^2 = 53 \times 10^{-6} \mu\Omega \text{ cm/K}^2$ for Au-0.2 at.% V we find $T_K = 1.14 \Delta = 250 \text{ K}$ which is a very reasonable value, compared to the estimate from the specific heat in section II.8.1.

It may be that magnetic Vanadium-oxides in the dilute alloys play the role of magnetic impurities, causing the positive deviations from the straight lines in fig. II.14 at the lowest temperatures. It should be noted however that these deviations are only weakly depressed by an external magnetic field.

Unknown impurities cannot account for the increase of $\rho(1 \text{ K})/\rho(4 \text{ K})$ with V-concentration. This increase is, as remarked before, similar to the concentration-dependence of the Cu-Fe resistivity shown in fig. II.10. We suggest a similar interpretation. Thus, interacting V-atoms may act as a pair with a lower effective Kondo-temperature. This idea is supported by the magnetoresistance. For alloy IV of fig. II.14 we observe a decrease of the slope of the ρ vs T^2 curve upon applying a magnetic field of 18 kOe ($\ll H_K$ for Au-V).

Our interpretation of the concentration dependence of the Au-V resistivity is in contrast to the interpretation of the concentration-dependence of the magnetic susceptibility^{135,129}) and of the V^{51} N.M.R. Knight-shift in Au-V alloys¹³⁴). Souletie and Tournier¹²⁹) report an analysis of the susceptibility by means of the sum of two Curie-Weiss relations, with two Curie-Weiss temperatures T_1 and T_2 . $T_1 \approx 225 \text{ K}$ should belong to isolated V-atoms and $T_2 \approx 1120 \text{ K}$ to non-isolated V-atoms. If this interpretation were correct, we should have observed $\Delta\rho \sim T^2$ for a wide range of V-concentrations in Au. Since we did not, we believe that the analysis of both N.M.R. and magnetic susceptibility results on Au-V should be reconsidered, in particular at concentrations below 2 at.% V.

II.9. Conclusions; remaining questions

Our main conclusions were already given in section II.1. We make a few additional remarks. We have provided considerable evidence that both the resistivity and the specific-heat approach their zero-temperature value as simple power-laws of the temperature. The consistency between the T_K -values determined from ρ and C supports this statement for both Cu-Fe and Au-V. Theoretically the conclusion that simple power laws govern the limiting low-temperature dependence of various physical properties was recently achieved by Anderson et al.⁹¹) for the s-d exchange model and by Hamann for Anderson's model¹⁴⁰). These theories have not been worked out so far as to allow a comparison with our results. Besides they only treat the spin 1/2 case.

Deviations from simple power-law behaviour in Cu-Fe could be accounted for assuming the presence of magnetic Fe-atom pairs with $T_K \approx 0.1 \text{ K}$, in quantitative agreement with experimental results of other authors. A straightforward interpretation of V-V interaction effects in Au-V is not yet possible.

It is very likely that a correct theory of low-temperature anomalies in the

transport properties should come out with a t-matrix of the form predicted by Nagaoka. The experimental results on resistivity and specific heat were most conveniently analyzed within the framework of Nagaoka's results^{31,110,130}. This is also the case for the thermopower and the Lorenz number (chapter III) and even for the apparent low-temperature concentration-dependence of T_K (fig. II.7). This concentration-dependence would then be associated with a great coherence-length however. Here we are faced with a contradiction because a long-range negative impurity spin-conduction electron spin correlation was not observed¹¹²). Even the existence of Heeger's quasiparticle is questionable. We have shown, in agreement with Tholence and Tournier, that at 460 ppm Fe in Cu (the alloy studied by Golibersuch and Heeger¹⁰⁰) an appreciable fraction of magnetic Fe-pairs is present. With this knowledge in mind a reinterpretation of the N.M.R. and Mössbauer results seems in order.

It would be very interesting to know if not yet a long-range spin-correlation — not necessarily negative — exists. Or to put it more generally, in view of our results, to learn more about the conditions for magnetism of two impurities in a metal as a function of their distance. We shall see in chapter IV that this problem is also of high interest as regards Pd-Cr and Pt-Cr dilute alloys.

A brief comparison with spinfluctuation theory may be useful. We shall evaluate the expression $\xi = (\chi d\gamma/dc) (\gamma d\chi/dc)^{-1}$ for Au-V and Cu-Fe; χ and γ are the host-susceptibility and electronic specific heat coefficient; $d\chi/dc$ and $d\gamma/dc$ are the impurity contributions per at.%. For Au-V we have $d\chi/dc = 45 \times 10^{-6}$ e.m.u./mol at.%¹³⁷). Let us evaluate T_K by means of the expression $d\chi/dc = \mu_{\text{eff}}^2 / 3 k_B T_K$. With $\mu_{\text{eff}} = 3 \mu_B$ ⁵⁷) we obtain $T_K = 250$ K, which is again in very good agreement with resistivity and specific heat. According to our analysis of the specific heat by means of Nagaoka's expression we write $d\gamma/dc = 2\pi/3 \Delta \approx 2.39/T_K$. If we assume $\chi = \mu_B^2 N(E_F)$ and $\gamma = \pi^2 N(E_F)/3$ (i.e. no enhancement effects in the host; the temperature is expressed in units of energy) we obtain $\xi = 2.2 \mu_B^2 / \mu_{\text{eff}}^2$. Thus for Cu-Fe $\xi = 0.16$ and for Au-V $\xi = 0.24$ ($\mu_{\text{eff}} = 3.7 \mu_B$ for Cu-Fe and $3.0 \mu_B$ for Au-V). According to Caroli et al.¹³⁶) $\xi = 3/2 (2\ell + 1) = 0.33$ ($\ell = 2$). The agreement is quite good. Better estimates are not possible. In particular the low-temperature value of the magnetic susceptibility of Cu-Fe is a difficult experimental problem.

The spinfluctuation temperature¹³⁶) is expressed by $T_{\text{sf}} d\chi/dc = 2 \mu_B^2 (2\ell + 1) / \pi k_B$, so that $T_{\text{sf}} \approx 9.5 (\mu_B / \mu_{\text{eff}})^2 T_K$. Thus T_{sf} and T_K are of the same order of magnitude for both Cu-Fe and Au-V.

Finally we want to emphasize that unfortunately we have not observed effects being proportional to the impurity concentration in Cu-Fe nor in Au-V. We doubt if anyone else has, with regard to the Kondo-effect. But in view of the analysis of the concentration dependence in the Cu-Fe system we have confidence that our conclusions regarding non-interacting magnetic impurities are correct.

Appendix I.

We shall evaluate the possible effect of deviations from Matthiessen's rule on the determination of T_K from $d\rho/d(T^2)$ in section II.6. We assume a transport relaxation-time of the form

$$\tau_1 = A(E) (1 + F(\omega)) \quad (\text{A.1})$$

for the magnetic impurities (i.e. Fe). We assume that the host (Cu) also contains impurities, described by a relaxation-time

$$\tau_2 = B(E) \quad (\text{A.2})$$

We neglect the small temperature dependence of the resistivity of pure copper.

$A(E)$ and $B(E)$ are assumed to be slowly varying functions of the energy. ($B \gg A$). $F(\omega) \ll 1$ is rapidly varying near $\omega (= E - E_F) = 0$, $\sim \omega^2$ for example, and causes the temperature-dependence of the resistivity. For the separate conductivities we have

$$\sigma_1 = - \int A(E) (1 + F(\omega)) G(E) \frac{\partial f}{\partial \omega} d\omega = AG(1 - \int F(\omega) \frac{\partial f}{\partial \omega} d\omega) \quad (\text{A.3})$$

$$\sigma_2 = - \int B(E) G(E) \frac{\partial f}{\partial \omega} d\omega = BG \quad (\text{A.4})$$

The function G accounts for energy-dependent quantities appearing in the transport integral. Slowly varying functions of E were taken out of the integral by their value at $E=E_F$. The total relaxation-time is obtained from

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}; \quad \tau = \frac{BA}{B+A} \frac{1 + F(\omega)}{1 + \frac{A}{B+A} F(\omega)} \quad (\text{A.5})$$

assuming the impurities scatter independently. The total conductivity is

$$\sigma = - \frac{BAG}{B+A} \int \left(1 + F - \frac{A}{B+A} F + \frac{A^2}{(B+A)^2} F^2 - \frac{A}{B+A} F^2 + \dots \right) \frac{\partial f}{\partial \omega} d\omega \quad (\text{A.6})$$

up to second order in F . The deviation from Matthiessen's rule is $\Delta M = \rho - \rho_1 - \rho_2 = \sigma^{-1} - \sigma_1^{-1} - \sigma_2^{-1}$. If this is worked out to second order in F one obtains

$$\Delta M = \frac{1}{G(A+B)} \left[\left(\int F \frac{\partial f}{\partial \omega} d\omega \right)^2 - \int F^2 \frac{\partial f}{\partial \omega} d\omega \right] \quad (\text{A.7})$$

If we assume that F is an even function of ω we have

$$\Delta M = \frac{1}{G(A+B)} \frac{52}{360} \pi^4 (k_B T)^4 (F''(0))^2 \quad (\text{A.8})$$

$$\text{Furthermore } \frac{1}{\rho_1(0)} \frac{d\rho_1(0)}{d(T^2)} = \frac{\pi^2}{6} k_B^2 F''(0) \quad (\text{A.9})$$

$$\text{so that } \frac{\Delta M}{\rho_1(0)} = \frac{A}{A+B} \frac{52}{10} \left(\frac{1}{\rho_1(0)} \frac{d\rho_1}{d(T^2)} T^2 \right)^2 \quad (\text{A.10})$$

The relative effect on the T^2 -term in the resistivity is

$$\frac{\Delta M}{\rho_1(0)} / \frac{1}{\rho_1(0)} \frac{d\rho_1}{d(T^2)} T^2 = \frac{A}{A+B} \frac{52}{10} \frac{1}{\rho_1(0)} \frac{d\rho_1}{d(T^2)} T^2 \quad (\text{A.11})$$

This is largest for Cu-30 ppm Fe, namely 7×10^{-4} at 1 K and can thus be neglected.

Appendix II

The possibility should not be excluded that size effects could be observed in the temperature dependence of the Cu-Fe resistivity. One attempt to measure such effects has been reported by Kitchens and Trousdale¹³⁸, but results have not been published. If a coherence length $\hbar v_F / \Delta = 6000 \text{ \AA}$ would exist in Cu-Fe this would be 0.6 % of the diameter of our specimens (0.1 mm) so that appreciable effects cannot be expected. As discussed before there is not much experimental and theoretical support for a great coherence length anymore. We shall nevertheless compare with each other some results on the Cu-Fe resistivity by several authors, were it only to demonstrate the possible variations in the measured magnitude of the temperature-dependence. In table II.6 results by four groups of authors are given. There is no obvious

Table II.6

Authors	Fe-conc.	$\rho(0 \text{ K}) / \rho(9 \text{ K})$
de Jong et al. ¹³⁹ rod, 3 mm diam.	100	1.065
	75	1.064
Daybell et al. ⁵¹ sphere, 11 mm diam.	63	1.076
	22	1.069
Loram et al. ⁶⁵ strip, 0.08 mm thick	400	1.09
	90	1.061
present work wire, 0.1 mm diam.	50	1.083

systematic variation of $\rho(0\text{ K})/\rho(9\text{ K})$ with sample dimensions. The difference between Loram's two alloys is probably caused by interaction effects as discussed in section II.6. The other differences are probably due to differences in sample preparation. We do not understand however the difference between the results by De Jong et al.¹³⁹ and our Cu-50 ppm Fe specimen, since these alloys were prepared in very much the same manner.

A straightforward application of the results given in table II.2 to resistivity results of others is apparently not possible. This is of importance in connection with the analysis of measurements of the Lorenz number, to be discussed in chapter III.

CHAPTER III

LORENZ NUMBER AND THE KONDO-EFFECT

III. 1 Introduction

First of all we shall define the Lorenz number L . If ρ is the electrical resistivity, W is the thermal resistivity and T is the temperature, then $L = \rho / WT$. The resistivities refer to scattering of conduction electrons by impurities. So in actual cases W is obtained by subtracting the lattice thermal conductivity from the measured thermal conductivity, inverting the result and subtracting the 'ideal' thermal resistivity. The 'ideal' resistivity is caused by phonons which scatter electrons. In the dilute alloys discussed in this chapter the ideal electrical resistivity can be neglected in the temperature range considered ($T < 9$ K). The ideal thermal resistivity is an important term however.

In section I. 4 we mentioned our initial measurements of the thermal conductivity of Cu-Fe, which were started with the aim to demonstrate some type of magnetic ordering. If inelastic, spin-dependent, scattering of conduction electrons by magnetic impurities occurs, one expects the transport of heat to be affected more than the transport of charge. In particular small-angle inelastic scattering may restore thermal equilibrium, while being almost ineffective in restoring equilibrium of the electron gas after displacement in k -space by an electric field. At low temperatures one thus expects the Lorenz-number of a magnetically ordering dilute alloy to be smaller than the Sommerfeld-value

$$L_0 = \frac{\pi^2}{3} \left(\frac{k}{e}\right)^2 \text{ for elastic impurity scattering. For } T \rightarrow 0 \text{ } L \text{ approaches } L_0,$$

because inelastic electron scattering is more and more inhibited. The effect of magnetic ordering on L has recently been studied by Jha¹⁴¹) on Silver-Manganese alloys and indeed a decrease of L from L_0 with increasing temperature was observed.

In our first trial experiments on Cu-Fe we found WT to decrease more rapidly than ρ with increasing temperature i.e. L increases with the temperature contrary to what is expected on the basis of magnetic ordering effects. It turned out later that 'Kondo-scattering' could account for an increasing L .

III. 2 Theoretical results based on the s-d model

Most calculations with regard to the Kondo-effect have been restricted to the electrical resistivity. Also experimentally of all the transport properties the electrical resistivity has been investigated most extensively. Indeed, precise measurement of a potential difference is much easier than precise measurement of a temperature difference.

Suhl and Wong³⁰) have numerically calculated the resistivity, the thermopower and the Lorenz-number using Suhl's dispersion theoretical solution of the s-d scattering problem. Fischer⁶⁹) calculated the three transport coefficients by

including potential scattering in the exact Bloomfield-Hamann solution⁶⁸) of Nagaoka's equations. Fischer simplified the problem by assuming the potential scattering to be large compared to the exchange scattering. This reduces the relative temperature dependence of all transport properties, and makes the temperature-dependence of the thermopower and the Lorenz-number indistinguishable from the effect of normal impurities. Besides, Fischer's calculation is only valid for $|\ln(T/T_K)| \gg 1$. Nam¹⁴²) also calculated the Lorenz-number, by expanding Hamann's solution of the t-matrix in terms of the energy.

It has been shown by Schotte¹²⁰) that Hamann's and Suhl's solution are nearly equal, and even identical if a particular density of states function is chosen. In section I. 7 we demonstrated that Hamann's solution does not describe the low-temperature properties of dilute magnetic alloys very well. Qualitatively however, and if $T > T_K$ the results may give a reasonably good picture. Therefore, in order to show what may be expected for the thermopower and the Lorenz-number we performed some numerical calculations using Hamann's solution⁶²). We introduced potential-scattering in the same simplified way^{120, 143, 144}) as in section II.5.2 and thus obtained a 't-matrix':

$$t(\omega) = \frac{1}{2\pi i \rho_1} (1 - e^{2i\delta} \times [X^2 + S(S+1)\pi^2]^{-1/2}) \quad (\text{III. 1})$$

where $X = \ln \{ (T - i\omega)/T_K \}$. If $\rho_1 J \ll 1$ and $\rho_1 V \ll 1$ then $\delta \approx -\pi V \rho_1$ (V is the ordinary potential, J is the exchange constant). The transport coefficients are obtained using the relaxation-time, defined by $(2\tau)^{-1} = -e \text{Im } t(\omega)$ and computing the familiar transport integrals²⁰). Some results are shown in fig. III.1.

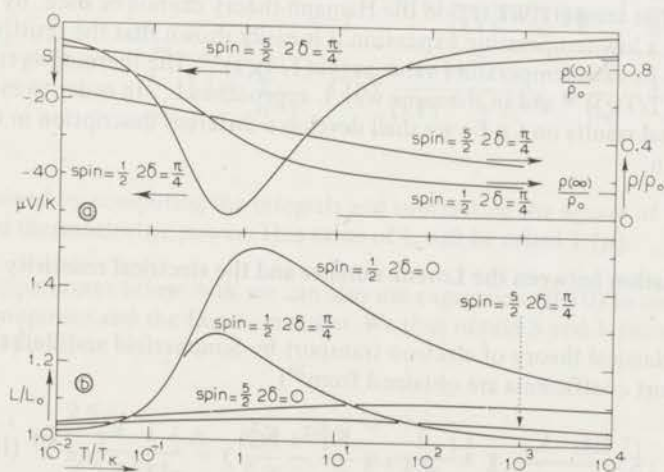


fig. III. 1 Some numerical results for the transport coefficients, computed with a relaxation-time obtained from (III.1)

a. **Resistivity (ρ).** The 'transition' occurs along a very wide temperature range, in particular for $\text{spin} = \frac{5}{2}$. In the latter case the curve is nearly a straight line. This was a main justification to use a $\ln T$ -term for the analysis in section II. 6.

ρ_0 is the unitarity limit, i.e. $3.8 \mu\Omega \text{ cm/at.}\%$ impurity for Copper. This is the zero-temperature limit of ρ if $\delta = 0$ for any spin value. If $\delta \neq 0$ then $\rho(0) = \rho_0 (1 + \cos 2\delta)/2$ and $\rho(\infty) = \rho_0 (1 - \cos 2\delta)/2$. This has been indicated by horizontal bars in fig. III.1.a for $2\delta = \frac{\pi}{4}$. Resistivity curves for $\delta = 0$ are similar to curves for $\delta \neq 0$, except for the limits at $T = 0$ and $T = \infty$. The curve for $\delta = 0$ and spin $\frac{1}{2}$ has been shown in fig. I.7. If $2\delta > \pi/2$ the resistivity increases with temperature. This looks like the behaviour of Rh-Fe, but, as remarked in section I.10., this is probably not the appropriate interpretation of the Rh-Fe resistivity.

Thermopower (S). Experimentally the largest peak-values observed are $\pm 20 \mu\text{V/K}$. The minimum for spin $\frac{1}{2}$ and $2\delta = \pi/4$ is thus rather deep. The minimum for spin $5/2$ is very broad, just as the resistivity-'transition'. If $\delta = 0$ then $S = 0$. If δ reverses sign so does S , whereas the resistivity curve does not change.

b. Lorenz-number ($L; L_0$ is the Sommerfeld-value). A peak occurs in the vicinity of $\ln(T/T_K) = 0$ just as for the thermopower and for the slope of the resistivity curve. Even far above T_K the Lorenz-number may be appreciably larger than the Sommerfeld-value. A small amount of potential-scattering appreciably suppresses this deviation however. Jha¹⁴¹) observed the Lorenz-number of an Ag-Mn dilute alloy (50 ppm Mn) to be 4% higher than L_0 from 0.6 – 3 K (well above T_K , which for Ag-Mn is probably < 0.01 K).

For an alloy with a resistance minimum we may thus expect to observe a maximum in L at a temperature $T \approx T_K$, whereas $L \rightarrow L_0$ if $T \rightarrow 0$. In this chapter we will be interested in the temperature-dependence of L for $T < T_K$ in Cu-Fe. In that temperature region the Hamann-theory cannot be used. By performing a low-temperature expansion it is easily shown that the resistivity approaches its zero-temperature value as $(\ln(T/T_K))^{-2}$. The thermopower goes to zero as $(\ln(T/T_K))^{-3}$ and in the same way L approaches L_0 . In order to interpret the experimental results on Cu-Fe we shall develop a different description in the next section.

III. 3 Relation between the Lorenz-number and the electrical resistivity

In the classical theory of electron transport by Sommerfeld and Bethe⁷⁾ the transport coefficients are obtained from²⁰⁾

$$\sigma = e^2 K_0; S = \frac{1}{eT} \frac{K_1}{K_0}; L = \frac{1}{e^2 T^2} \left(\frac{K_2}{K_0} - \frac{K_1^2}{K_0^2} \right) = \frac{1}{e^2 T^2} \frac{K_2}{K_0} - S^2 \quad (\text{III.2})$$

K_n are the transport integrals, which for the present case can be written:

$$K_n = -C \int_{-\infty}^{+\infty} \tau(\omega) \omega^n \frac{\partial f}{\partial \omega} d\omega \quad (\text{III.3})$$

where C is a constant. τ is the relaxation time and $\omega = E - E_F$. By means of the

Sommerfeld expansion the transport coefficients can be developed in a powerseries of the temperature. One obtains

$$K_n/C = [\omega^n \tau + \frac{(\pi k T)^2}{6} (\omega^n \tau)'' + \frac{7(\pi k T)^4}{360} (\omega^n \tau)'''' + \dots]_{\omega=0} \quad (III.4)$$

This expansion can be used to express the temperature dependence of the Lorenz-number in terms of the temperature dependence of the resistivity. Up to order T^2 :

$$L = L_0 \left[1 - \frac{32}{10} \frac{T^2}{\rho(0)} \frac{d\rho}{d(T^2)} \right] - S^2 \quad (III.5)$$

In principle this expansion can be continued to any arbitrary order in T^2 . The Lorenz-number is thus uniquely determined by the electrical resistivity and the thermopower. The expansion is exact as far as transport properties can be described by an energy- (or even wave vector-) dependent relaxation-time in an independent (not necessarily free) electron model. The relaxation-time should not be temperature-dependent however.

The best way to check the relation between the Lorenz-number and the electrical resistivity is to construct a numerical representation of resistivity measurements. We have described such a representation in section II.5.1, formula (II.4). With the same constants $C(n)$ we have

$$L + S^2 = \frac{1}{e^2 T^2} \frac{\int_{-\infty}^{+\infty} x^2 T^2 \left[1 + \sum_{n=1}^6 C(n) \frac{(xT)^{2n}}{(xT)^{2n+\Delta} 2^n} \right] \frac{\partial f}{\partial x} dx}{\int_{-\infty}^{+\infty} \left[1 + \sum_{n=1}^6 C(n) \frac{(xT)^{2n}}{(xT)^{2n+\Delta} 2^n} \right] \frac{\partial f}{\partial x} dx} \quad (III.6)$$

L is obtained by computing the integrals and subtracting the square of the measured thermoelectric power. This value of L will be called $L(\rho)$.

At temperatures below $\approx 4K$ we can also use expression (II.10) to compute the thermopower and the Lorenz-number. We thus obtain S and L from (III.2) and (III.3) with

$$[\tau(\omega)]^{-1} = \frac{2Sc}{\pi\rho_1} \left[A - \text{Re} \left(e^{2i\delta} \frac{\omega - i\Delta}{\omega + i\Delta} \right) \right] \quad (III.7)$$

which follows from (II.10). (S is the spin of the impurity). In fig. III.2 we show some results. The 'Hamann'-curve has been included to demonstrate the difference in temperature dependence below 1 K. The choice of spin $\frac{1}{2}$ and $2\delta = \pi/4$ is arbitrary, but the low-temperature slope is characteristic.

$T_K = 20 K$ was chosen in view of our analysis in section II.6.

The curve for $L(\rho)$ in fig. III.2 has a maximum at $T = 13.5 K$, i.e. the same

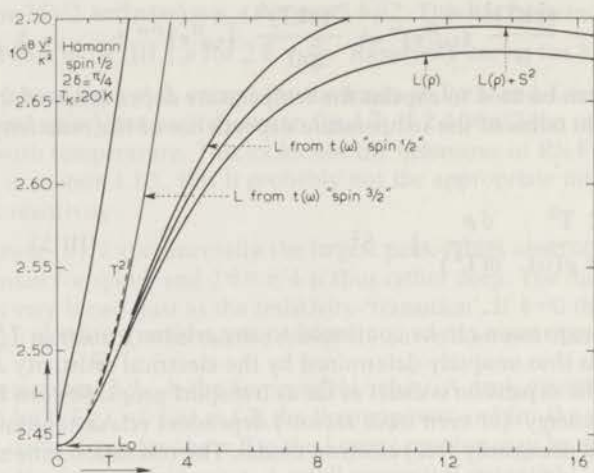


fig. III.2 Various numerical results for the Lorenz-number. The 'Hamann'-curve obtained with (III.1) approaches L_0 with a very steep slope. The other curves are for Cu-Fe. $L(\rho)$ is computed with (III.6) and the constants from table II.2. Also shown is L as obtained with (III.7) and the constants from table II.3, case III and IV ('spin $\frac{1}{2}$ ' and 'spin $\frac{3}{2}$ '). The dashed line is the extrapolation of (III.5), S^2 not subtracted. S is the measured thermoelectric power.

order of magnitude as the estimated T_K -value. Although in principle our evaluation of L is exact, the actual form which we choose for the empirical relaxation time (II.4) may influence the final result. This depends on the precision of the resistivity measurement and the accuracy of the representation by the empirical relaxation time. Both were very good (section II.5.1.).

In section II.5.2 we have seen that with the 't-matrix' $t(\omega)$ as defined in expression (II.10) the resistivity of Cu-Fe is described reasonably well up to 4 K (fig. II.5, curve III). We have calculated the Lorenz-number with the same constants, as defined in section II.5.2., and the same relaxation time (III.7). Below 4 K the agreement between L from $t(\omega)$ ('spin $\frac{1}{2}$ ') and $L(\rho)$ is reasonably good. Above 4 K the curve should not be taken too seriously but the agreement with $L(\rho)$ is not really poor. In section III.4 we shall see that also the thermopower can be described well by using the relaxation-time (III.7). We finally notice that 'spin $\frac{3}{2}$ ' in fig. III.2 is in poor agreement with $L(\rho)$. In fig. II.5 we saw that also the resistivity is poorly described in this case.

III. 4 Experimental results on Copper-Iron

In this section we shall compare our phenomenological theory with experimental results on Cu-Fe. As far as we know the Lorenz number of Cu-Fe

has never been measured. We shall not describe the apparatus nor the analysis of the experimental data, but only show the final results *). In table II.6 we have seen that $\rho(0\text{ K})/\rho(9\text{ K})$ of our Cu-50 ppm Fe specimen is larger than $\rho(0\text{ K})/\rho(9\text{ K})$ of the Cu-Fe specimens on which the Lorenz-number was measured. So we cannot directly compare the curve of $L(\varphi)$ as shown in fig. III.2 with the experimental results. We have therefore analysed the resistivity measurements, which were performed to obtain the Lorenz-number, in the same way as Cu-50 ppm Fe, with expression (II.4), i.e.

$$\frac{\sigma(T) - \sigma(0)}{\sigma(0)} = - \sum_{n=1}^m C(n) \int_{-\infty}^{+\infty} \frac{(xT)^{2n}}{(xT)^{2n} + \Delta^{2n}} \frac{\partial f}{\partial x} dx \quad (\text{II.4})$$

σ is the electrical conductivity.

We choose $m=4$. A T^5 -term for the Cu-lattice resistivity like in (II.5) was not included because the measurements were not performed above 9 K, at which temperature the lattice resistivity of Cu is still negligible.

We have also determined the constants in $\tau(\omega)$ from the analysis of the resistivity results by de Jong et al. by means of (III.7). We recall that the three constants to be determined are obtained from (II.11 a, b, c), i.e. the resistivity at $T=0$, $d\rho/d(T^2)$ and the thermopower, which was taken to be $-3\mu\text{V/K}$ at 1 K. The results of the analysis are given in table III.1. The measured resistivity values were scaled to the resistivity of Cu-50 ppm Fe as discussed in section II.5 (table II.2). The fact that $C(1)$ of table III.1 is somewhat smaller than $C(1)$ of table II.2 reflects the difference between the two Cu-Fe specimens as remarked above and in connection with table II.6. The values of Δ , δ and A on the right hand side of table III.1 also differ somewhat from the corresponding values in table II.3 (case III). The thermoelectric power, computed with (III.3), (III.7) and the constants from

Table III. 1

Analysis of resistivity with (II.4) $\rho(0) = 0.057369 \mu\Omega \text{ cm}; \Delta = 21.25 \text{ K}$	Coefficients of (III.7) 'spin = $\frac{1}{2}$ '		
	Δ (K)	δ	A
$m=4$; r.m.s. $\Delta\rho/\rho = 1.6 \times 10^{-4}$		2.8	
$C(1) = 3.08264621227\text{E}-01$	20.75	0.729	5.33
$C(2) = -1.73941563971\text{E}-01$			
$C(3) = 1.27783033034\text{E}-01$			
$C(4) = 2.51654963096\text{E}-03$			

Specimen: Cu-100 ppm Fe; rod, 3 mm diameter

*) The experiments and their analysis are the graduate work of P.C.M. Gubbens and J.J. de Jong. This work will be published together with the present author¹³⁹).

table III.1 is compared with experimental results in fig. III.3. The agreement is very good, even above 4 K, where, according to the comparisons made in fig. II.5 and III.2, the description of ρ and L by the empirical 't-matrix' is a little poorer. Actually, the agreement above 4 K is too good because our empirical 't-matrix' (II.10) is an extension of Nagaoka's result. If this extension has a meaning it will be for $T < T_K$.

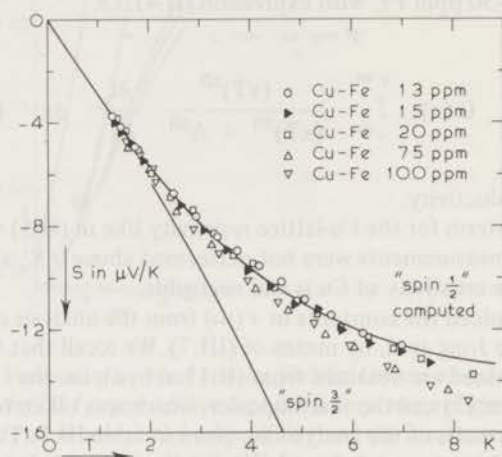


fig. III.3 Thermoelectric power of some dilute Cu-Fe alloys. The computed curve was obtained with the constants from table III.1. The curve for 'spin $\frac{3}{2}$ ' (table II.3, case IV) deviates rather strongly. The same is true for the resistivity as shown in fig. II.5, curve II, and for the Lorenz-number, as shown in fig. III.2.

Just like we have seen in fig. II.5 for the resistivity, also for the thermoelectric power a spin-value of $\frac{1}{2}$ substituted in (III.7) gives a much better description of the experimental results for $T < T_K$ than a spin-value of $\frac{3}{2}$. It should be emphasized that one point of the thermopower-curve has been used to calculate the constants of table III.1.

In order to compare the predicted temperature-dependence of the Lorenz-number with experimental results on Cu-Fe, one should know L at $T=0$ for pure Copper. The most reliable value of L for pure copper available at this moment is probably Schriempf's value of $2.48 \times 10^{-8} \text{ V}^2/\text{K}^2$ (145). De Jong et al. (139) could infer from their experimental results the same Lorenz-number for Cu as Schriempf did. However, from an analysis of Lorenz-number measurements on some dilute nonmagnetic Cu-Ge and Cu-Sn alloys the Sommerfeld-value of $2.443 \times 10^{-8} \text{ V}^2/\text{K}^2$ was found to be in better agreement with the experimental results. Schriempf reports a weak resistance minimum in his pure copper. De Jong et al. also found a weak resistance minimum in pure Copper and concluded that the impurities causing this minimum are probably also responsible for the

deviation of L from the theoretical value. This is satisfactory because the fact that L of pure Copper is equal to the Sommerfeld-value supports the description of electron transport properties in Copper by a Boltzmann equation in an independent electron model.

A straightforward comparison of experiment and theory is now possible. Fig. III.4 shows experimental results on some dilute Cu-Fe alloys compared with $L(\rho)$. The scatter of the points for each concentration is small. The relative precision of the measurements is better than 0.5%¹³⁹). One notices

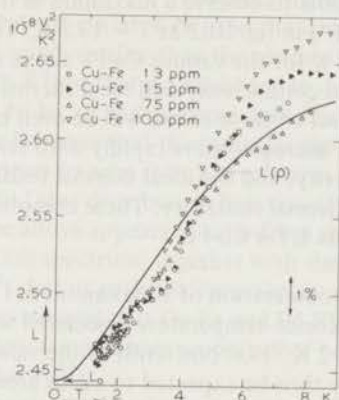


fig. III.4 Comparison of experimental values for the Lorenz-number of some dilute Cu-Fe alloys with $L(\rho)$. (constants from table III.1).

that below 5 K the values of L for the various Fe concentrations do not differ by more than 1%. Above 5 K the differences become greater although at 8.5 K the maximum difference is still not more than 2% of L . Two uncertainties are contained in the experimental results of fig. III.4. The first is the lattice thermal conductivity, which was subtracted from the measured thermal conductivity to obtain the electronic thermal conductivity. The lattice thermal conductivity was assumed to be the same for all four Cu-Fe alloys (probably correct) and proportional to T^2 up to 9 K (uncertain). The second uncertainty is the value of the ideal thermal resistivity of the alloy which was subsequently subtracted from the total electronic thermal resistivity, in order to obtain the thermal resistivity caused by the Fe-atoms. A unique value cannot be determined because deviations from Matthiessen's rule which occur in the 'ideal' electrical resistivity (fig. I.3) are even larger in the 'ideal' thermal resistivity. Estimates for the ideal thermal resistivity of the Cu-Fe alloys were obtained from thermal conductivity measurements on nonmagnetic Cu-Sn and Cu-Ge alloys. The experimental Lorenz-number values above 5 K in fig. III.4 reflect the errors in these estimates. For Cu-100 ppm Fe the corrections and thus the possible errors are largest.

At 3 K all points lie below $L(\rho)$. The deviation is smaller than 1% of L however and may be combined result of small errors in the estimated lattice thermal conductivity, the ideal thermal resistivity and the measurements.

We conclude that $L(\rho)$ describes the Lorenz-number of Cu-Fe alloys quantitatively within the accuracy of the analysis of the experimental results.

III. 5 Conclusions and prospects

We have demonstrated that the information necessary to describe the temperature dependence of the Lorenz-number of Cu-Fe is contained in the resistivity and the thermoelectric power. Of course the validity of this conclusion is limited by the uncertainties in the experimental results and their analysis. The conclusion is of fundamental importance because it after all justifies our use of the classical electron transport theory, within the independent electron model. It will probably not be possible to observe a maximum in the Lorenz-number of Cu-Fe as exhibited by $L(\rho)$ in fig. III.2 at $T = 13.5$ K. The differences between values of L at $T=8$ K for the various Cu-Fe alloys reflect the errors in the estimated lattice thermal conductivity and ideal thermal resistivity. At higher temperatures the effect of these errors will be even larger because the lattice thermal conductivity increases more rapidly with temperature than the electronic thermal conductivity, and the ideal thermal resistivity increases more rapidly than the impurity thermal resistivity. These complications inhibit the observation of a maximum in L for Cu-Fe.

A possible candidate for observation of a maximum in L as a function of temperature is Cu-Cr. The Kondo-temperature associated with Cr in Cu has been estimated to be about 2 K^{13} i.e. one tenth of the value for Fe in Cu. A maximum value of L may thus be expected to occur around 2 K, if we compare figs. III.1 and III.2. This offers an interesting possibility to further test the relation between L and ρ . Very precise measurements of ρ will then be needed however, down to very low temperatures such as described for Cu-Fe in Chapter II. Very precise measurements of the thermal conductivity are also necessary, which is difficult below 1 K.

The maximum value of L for Cu-Fe in fig. III.2 lies 10 % above L_0 . We presume that in Cu-Cr the maximum value of L will be appreciably larger. The reason for this conjecture is that the thermoelectric power and the resistivity of Cu-Cr suggest that the ratio of exchange scattering to potential scattering in Cu-Cr is larger than in Cu-Fe. The thermoelectric power of Cu-Cr is not anomalously large, but about thirty times smaller than the value of Cu-Fe at 1 K^{147}). In the picture of the s-d model this means that δ is small (fig. III.1), in qualitative agreement with the fact that the 'step'-value of the Cu-Cr resistivity (from $T=0$ to $T \gg T_K$) is appreciably larger than in Cu-Fe¹¹⁸). This is also in agreement with the virtual bound state picture according to which the upper half of the virtual bound state of Fe in Cu crosses the Fermi surface, so that the $\ell=2$ phase-shifts are large. On the other hand it has been proposed¹⁴⁷) that the two halves of the virtual bound state of Cr in Cu lie symmetrically relative to E_F so that there is no appreciable resonance scattering, and the $\ell=2$ phase shifts are smaller.

Formula (III.5) predicts an increase of L with increasing temperature when the impurity resistivity shows a negative T^2 -term at low temperatures (Kondo-effect)*. On the other hand there exist also dilute alloy systems, showing a positive T^2 -term in the low-temperature resistivity. In that case L should decrease with increasing temperature. An example is Ni in Pd. A straightforward application of (III.5) to Pd-Ni is probably not possible however.

* For the cases which we consider S^2 can be neglected if $T \ll T_{s,f}$.

The T^2 -term in the resistivity of pure Pd results from scattering of s-conduction-electrons by heavy d-electrons. At zero temperature this resistivity-contribution is also zero. A transport relaxation-time appropriate to pure Pd would be infinite at $T=0$. Thus for calculations of the pure-Pd T^2 -term, and also of the T^5 lattice-term, a variational method is used^{5,73} instead of an energy-dependent relaxation-time in a transport integral like (III.3). Ni is isoelectronic with Pd so that the residual resistivity caused by Ni in Pd is small. Calculations of the positive T^2 -term which Ni contributes in Pd have thus also been performed by means of a variational method^{73, 148}. However, the residual resistivity of Ni in Pd is not zero (about $0.4 \mu\Omega \text{ cm/at. \% Ni}$) and the contribution of the T^2 -term below 10 K is much smaller than the residual resistivity (about $250 \times 10^{-6} \mu\Omega \text{ cm/at. \% K}^2$) so that we might try to describe the Ni contribution to the resistivity of Pd-Ni by an energy-dependent relaxation-time. We must nevertheless emphasize however that theoretically the T^2 -term in the resistivity of Cu-Fe appears to arise from the ω^2 -term in the relaxation-time, together with the Fermi-Dirac distribution function (II.3). The T^2 -term in the resistivity of Pd-Ni type alloys appears to arise from the ω^2 -dependence of the spinfluctuation excitation spectrum, together with the Bose-Einstein distribution function⁷³). Let us nevertheless make a comparison, in view of the fact that it is sometimes stressed that Cu-Fe and Pd-Ni type alloys should be equivalent in that the low-temperature properties of both should be described by a spin fluctuation theory⁷³).

Schriempf et al. have studied the Lorenz-number of Pd-Ni both experimentally and theoretically¹⁴⁸). The electrical resistivity is written as

$$\rho = \rho(0) + AT^2 + BT^5 \quad (\text{III.8})$$

$\rho(0)$ is the residual resistivity; the T^2 -term is the combined result of s-d scattering in the Pd-host and on the Ni-impurity. The T^5 -term describes the lattice resistivity. The thermal resistivity reads

$$W = c/T + \alpha T + \beta T^2 \quad (\text{III.9})$$

The first term on the right hand side is the impurity-scattering term, the second is the electron-electron scattering term and the third term is the ideal thermal resistivity (electron-electron scattering in the Pd-host, as well as impurity induced electron-electron scattering occur in Pd-Ni). The Lorenz-number for electron-electron scattering is defined as $L_e = A/\alpha$.

The scattering process in the Kondo-effect is sometimes also visualized as an impurity-induced effective electron-electron interaction. Analogous to (III.8 and 9) we write

$$\rho = \rho(0) + \frac{d\rho}{d(T^2)} T^2 \quad (\text{III.10})$$

$$W = \frac{\rho}{LT} = \frac{\rho(0)}{L_0 T} + \frac{42}{10} \frac{T}{L_0} \frac{d\rho}{d(T^2)} \quad (\text{III.11})$$

using (III.5). The term $-S^2$ in L can be neglected*. The phonon-term has been

* $S \approx -10^{-6} \times T \text{ V/K}$ for Pd-Ni below 10 K¹⁵⁰) and $\frac{1}{\rho(0)} \frac{d\rho}{d(T^2)} = 6 \times 10^{-4} \mu\Omega \text{ cm/K}^2$

omitted. It follows from (III.10) and (III.11) that $L_e = \frac{10}{42} L_o = 0.6 \times 10^{-8} \text{V}^2/\text{K}^2$. Notice that the thermal resistivity due to the effective electron-electron scattering is negative in the case of a negative low-temperature T^2 -term in the electrical resistivity.

Our value of L_e is smaller than the value $L_e \approx 0.9 \times 10^{-8} \text{V}^2/\text{K}^2$ as obtained by Schriempf et al.¹⁴⁸) for Pd-Ni alloys using the model of localized spin fluctuations. But our value lies within the estimated maximum experimental error for the Pd-Ni alloys where impurity scattering dominates (0.5 and 1.0 at.% Ni of ref. 148).

The experimental values given by Schriempf et al. for L_e of Pd and Pd-Ni alloys are nearly independent of the impurity concentration, and the average value is $L_e = 1.2 \times 10^{-8} \text{V}^2/\text{K}^2$. This is twice the value obtained by us, which should be universal for scattering processes that can be described by an energy- (not temperature-) dependent relaxation time. But besides the fact that our value of L_e is within the experimental error for the alloys where impurity scattering dominates, Schriempf et al. find a nearly concentration-independent ideal thermal resistivity. It has been observed that the ideal thermal resistivity of Copper may increase by a factor of 10 upon addition of impurities¹³⁹). As such low-temperature deviations from Måthiessen's rule occur very generally we expect them to occur also in Pd-Ni alloys. Furthermore Schriempf et al. observe a coefficient B (III.8) for the phonon-resistivity which decreases with increasing Ni-concentration and even becomes negative for Pd-1 at.% Ni. This means that either Ni-atoms interact with each other or that the Ni-contribution to the electrical resistivity is not proportional to T^2 up to 10 K (fig. 3 of ref. 148). In the latter case the term αT (III.9) will probably neither be valid above 10 K, contrary to Schriempf's assumption. Finally it is questionable whether the lattice thermal conductivity and the ideal thermal resistivity are proportional to T^2 above 10 K, as the electrical lattice resistivity is proportional to T^5 only up to 10 K.

Thus, in summary, the possible errors in the experimental results are so large that it is not yet certain whether the Lorenz-number of Pd-Ni alloys provides any new information, not already contained in the electrical resistivity.

Recently Rice¹⁴⁹) calculated the electronic thermal resistivity within the model of localized spin fluctuations beyond the term αT of (III.9). According to this author salient features of the model would show up in the thermal resistivity. We believe that Pd-Ni is not the most appropriate system to test the theory, because the T^2 -term in the resistivity (and consequently α) are relatively small. One should rather take an alloy with a lower spin-fluctuation temperature like Rh-Fe. The spin-fluctuation temperature of Rh-Fe is of the same order of magnitude as the Kondo-temperature of Cu-Fe. As we have seen that the Lorenz-number of Cu-Fe can be calculated from the electrical resistivity and the thermoelectric power, it would be interesting to learn if Rh-Fe behaves similarly or differently in this respect.

Finally, the spin-fluctuation temperature of Pt-Co¹⁵¹) may be of the same order of magnitude as the Kondo-temperature of Cu-Cr, so that also measurement of L on Pt-Co in comparison with Cu-Cr may be worthwhile.

CHAPTER IV.

KONDO-EFFECT IN PALLADIUM-CHROMIUM AND PLATINUM-CHROMIUM ALLOYS

IV. 1. Phenomenological introduction

Palladium is a very complicated metal, as compared to Copper which was discussed as a host to Iron in the preceding two chapters. Like Copper, Palladium has a broad band of sp-electrons, with a relatively low density of states at the Fermi-energy (comparable to Copper). The sp-electrons are thought to carry most of the electric current. Additionally and contrary to Copper, Palladium has (grossly speaking) a narrow d-band which crosses the Fermi-surface and has a high density of states at E_F . The exchange interaction between electrons in the d-band is very large compared to the exchange interaction between sp-electrons. Due to the exchange interaction the paramagnetic susceptibility of the d-electrons is enhanced by a factor of 10 over the non-interacting case, and consequently Palladium is nearly ferromagnetic.

The band structure of Platinum is very much similar to that of Palladium. However, the exchange enhancement in the d-band is much weaker: $\approx 5/3$ *) for Pt as compared to 10 for Pd⁷³⁾.

The magnetic properties of transition-metal atoms are determined by the electrons in their d-shell. If transition-metal atoms are dissolved in Pd or Pt it is likely that the d-band of the host will be important to the magnetic state of the alloy. The effect of the Pd d-band becomes clear if we compare Au and Pd as a host to the first-row transition metal atoms. Elements from V to Co, when dissolved in Au, cause the resistance minimum phenomenon to occur, with Kondo temperatures ranging from $T_K < 10^{-3}$ K (probably) for Au-Mn to $T_K \approx 300$ K for Au-V and Au-Co. Au-Ni alloys are only magnetic (temperature-dependent magnetic susceptibility) above ≈ 10 at.% Ni. In Pd, the Ni-atom is also non-magnetic, but the local susceptibility at the Ni-sites is strongly enhanced, over the already enhanced susceptibility of the host itself. At concentrations above about 2 at.% Ni, Pd-Ni is ferromagnetic. Co and Fe in Pd have a magnetic moment *) and dilute Pd-Fe and Pd-Co alloys are ferromagnetic even at impurity concentrations below 0.1 at.%. The d-electrons of Pd are coupled ferromagnetically to Fe and Co in the vicinity of the impurity to form the so-called giant moments¹³¹⁾. Mn in Pd has also a magnetic moment and Pd-Mn alloys are also ferromagnetic even below 0.1 at.% Mn. (It is difficult to observe if, and below which concentration, ferromagnetism of Pd-(Mn, Fe, Co) dilute alloys disappears, since the Curie-temperature decreases to far below 1 K with decreasing impurity-concentration.) Mn only weakly polarizes the Pd-matrix. From magnetic-susceptibility measurements a magnetic moment of $5\mu_B$ is found. The specific heat of Pd-Mn alloys reveals a very peculiar type of magnetic ordering¹³¹⁾.

*) Andersen¹⁶⁶⁾ obtains 3.8 for the exchange enhancement factor of Pt.

*) The possibility should not be excluded that isolated Fe- and Co-atoms in Pd are nonmagnetic at $T = 0$, just as is observed for V in Au, Fe in Cu and is presumed for many other dilute alloys such as Fe in Au or Co in Pt.

V is nonmagnetic in Pd and causes no effects which would distinguish it from e.g. Ag or Mo.

Only Cr in Pd causes a resistance minimum analogous to V in Au or Fe in Cu. According to Moriya¹⁵²), if Cr in Pd has a magnetic moment, it will cause negative polarization of the host d-electrons relative to the impurity-moment. In contrast to Pd-Fe and Pd-Co this phenomenon has been called a 'dwarf' moment by Campbell¹⁵³).

First-row transition metals dissolved in Pt behave very much similarly to the equivalent Pd-alloys. Due to the smaller exchange enhancement of the susceptibility of Pt relative to Pd, the giant moments of Fe and Co in Pt are 'less giant' however. Cr in Pt again causes a resistance minimum.

The general behaviour of the electrical resistivity of Pd-Cr alloys is shown in fig. IV.1. The curves are completely analogous to electrical-resistivity curves of Cu-Mn and Au-Fe (see e.g. fig. I.6). Only the scales of temperature and

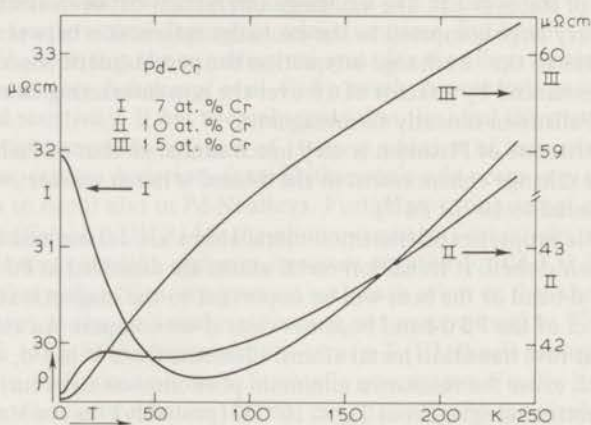


fig. IV.1 Electrical resistivity of some concentrated Pd-Cr alloys. We have not observed resistance minima above 100 K in Pd-Cr, in contrast to Au-V, where minima above room temperature have been observed. This may be due to the fact that the resistivity of Pd increases more rapidly with temperature than the resistivity of Au. Also, T_K of Pd-Cr may be lower than T_K of Au-V (see however section IV.4)

impurity-concentration are different. The fact that both a resistance minimum and a maximum are observed at relatively high temperatures is indicative of a relatively high Kondo temperature, higher than T_K of Cu-Fe for example.

Gainon and Sierro¹⁵⁴) observed a large positive thermoelectric power in Pd-Cr, with a maximum value of about $11 \mu\text{V/K}$ at 30 K. In general a maximum (positive or negative) of the thermopower is observed in the vicinity of T_K , so that T_K for Pd-Cr might be of the order of 30 K. The present author estimated $T_K=200 \text{ K}$ from electrical resistivity and specific heat of Pd-Cr alloys⁸³) Applying a formula obtained by Rivier and Zuckermann⁷⁵) from spinfluctuation theory to the thermopower at $T \ll 30 \text{ K}$, a value of $T_K \approx 200 \text{ K}$ was also estimated by Gainon and Sierro¹⁵⁶). The possible value of T_K for Pd-Cr will be reconsidered in section IV.4.

Clearly, Pd-Cr is a good candidate for studying the physical properties in the limit $T \ll T_K$, and so is Pt-Cr. In fig. I.8 and fig. I.10 we have already shown some preliminary results on the resistivity of dilute Pd-Cr and Pt-Cr alloys, indicating that the resistivity approaches as T^2 its zero-temperature value. In this chapter the temperature-dependence of resistivity, thermopower and specific heat will be discussed in some more detail. In particular, the concentration-dependence of the T^2 -term of the resistivity will appear to be very much similar to that of Cu-Fe (see fig. II.7 and table II.4).

Can we be sure that the Pd-Cr and Pt-Cr systems are analogous in all aspects to Cu-Fe or Au-V, or will the d-band of the host-metal considerably complicate the situation? If Cr in Pd or Pt has a magnetic moment at low temperatures we have to consider the negative polarization of the host, as calculated by Moriya¹⁵²). If, however, 'Kondo-condensation' (or whatever the phenomenon should be called) occurs at low temperatures Cr is nonmagnetic and we do not need to worry about polarization of the d-band.

We shall see in the following sections that macroscopically as yet nothing distinguishes Pd-Cr and Pt-Cr from other 'Kondo-alloys'. Thus $\Delta \rho \sim -T^2$, $\Delta C \sim T$, and the concentration-dependence of the apparent T_K -value is very much similar to Cu-Fe as shown in fig. II.7. Microscopic properties have only been investigated on Pt-Cr (i.e. N.M.R.); the few published data¹⁵⁵) again fit in well with data on similar systems, such as Au-V or Mo-Co.

Before presenting further our experimental results we shall give some experimental details. Work by other authors on Pd-Cr and Pt-Cr – not much of which has been published – will be discussed in relation to our own results in the appropriate sections.

IV. 2. Experimental details

IV.2.1. Alloy preparation

All Pd- and Pt-alloys were melted in Al_2O_3 crucibles in an induction furnace under Argon atmosphere. After solidification the alloys were annealed at $1000^\circ C$ in vacuum during 24 hours and subsequently quenched in water. Appropriate pieces were spark-cut from the alloy-buttons, rolled and drawn to wires of a diameter depending on the Cr-concentration (minimum diameter 0.1 mm). After drawing and mounting (section IV.2.2) the wires were reannealed to remove strains, and cooled slowly to room-temperature, by removing the furnace from the quartz-tube in which the wires were suspended.

The Pt-Cr wires were annealed at $600-800^\circ C$. The Pd-Cr wires were initially annealed at $800^\circ C$. We discovered however that annealing at this temperature caused a rather large residual resistivity of the pure Pd which had been purchased in the form of wire (W2231). We therefore lowered the annealing temperature of Pd and Pd-alloy wires to $600^\circ C$ and then observed residual resistivities which were in better agreement with the purity, or the nominal impurity-concentration. We had no problems with the residual resistivity of pure Pd-sponge (S8750).

Data regarding concentrations, annealing times, etc. are given in table IV.1 and table IV.2. In table IV.1 we notice that the nominal and the analysed

Table IV. 1

Alloy at.% Cr nominal	Melting time (min.)	Annealing after drawing		ρ (T=0) $\mu\Omega$ cm	$\Delta\rho/c_{nom.}$ $\mu\Omega$ cm/at.%	analysis at.% Cr	$\Delta\rho/c_{an.}$ $\mu\Omega$ cm/at.%
		hours	$^{\circ}$ C				
Pt-S3389	30	5	800	0.0125	—	—	—
Pt-0.5 Cr (1)	30	5	800	2.189	4.35	0.57	3.82
Pt-1 Cr	45	6	800	4.418	4.41	1.13	3.90
Pt-1 Cr	45	7	600	4.395	4.38	1.13	3.88
Pt-S8713	15	7	600	0.037	—	—	—
Pt-0.75 Cr (3)	15	7	600	3.278	4.32	0.89	3.64
Pt-1.5 Cr (3)	15	7	600	6.781	4.50	1.58	4.27
Pt-3 Cr	30	7	600	13.80	4.59	3.13	4.40

Analysis Pt-S3389 (Johnson & Matthey): 1 ppm Si, other elements less than 1 ppm
 Analysis Pt-S8713 (Johnson & Matthey): 3 ppm Si, other elements less than 1 ppm
 Cr: JM 2945. Numbers in brackets in the first column indicate the concentration
 of the master alloy. S = 'sponge'.

Table IV.2

Alloy at.% Cr nominal	Melting time (min.)	Annealing after drawing		ρ (T=0) $\mu\Omega$ cm	$\Delta\rho/c_{nom.}$ $\mu\Omega$ cm/at.%	analysis at.% Cr _c	$\Delta\rho/c_{an.}$ $\mu\Omega$ cm/at.%
		hours	$^{\circ}$ C				
Pd-S8750	15	18	600	0.068	—	—	—
Pd-0.1Cr (0.4)	15	19	570	0.531	4.63	0.11	4.21
Pd-0.2Cr (0.6)	15	18	600	0.850	3.91	0.18	4.34
Pd-0.4Cr (0.6)	15	18	600	1.377	3.27	0.38	3.44
Pd-0.6Cr	30	18	600	2.111	3.41	0.57	3.58
Pd-W2231	—	19	570	0.525	—	—	—
Pd-0.25Cr (3)a	30+8	3	850	1.735	4.84	0.206	5.87
Pd-0.25Cr (3)b	30+8	18	600	0.890	1.46	0.206	1.77
Pd-0.50Cr (3)	30+8	19	570	1.798	2.55	0.413	3.08
Pd-1 Cr (3)	30+8	19	570	4.184	3.66	0.86	4.25
Pd-3 Cr	30+8	19	570	13.03	4.17	2.71	4.61
Pd-7 Cr	30+8	4 $\frac{1}{2}$	800	31.94	4.49	6.55	4.80
Pd-10 Cr	30+8	4 $\frac{1}{2}$	800	41.49	4.10	9.20	4.45
Pd-15 Cr	30+8	4 $\frac{1}{2}$	800	56.43	3.73	14.20	3.94

Analysis Pd-S8750 (Johnson & Matthey): 8 ppm Si, other elements less than 1 ppm
 Analysis Pd-W2231 (J & M): 7 ppm Si, 4 ppm Fe, other elements less than 1 ppm
 Cr: JM 4898. Numbers in brackets in the first column indicate the concentration
 of the master alloy. S = 'sponge', W = 'wire'. '30+8' in the second column means:
 melted (30 min.), inverted and remelted (8 min.).

Cr concentrations are in reasonably good agreement with each other. The resistivity values per atomic % Cr show less scatter however when nominal concentrations are used. We observed the same for Cu-Fe in table II.1. The Cr-concentrations in Pt and Pd were determined by Johnson and Matthey Chemicals Ltd. The Cr-concentrations in Pd were also determined by Mr. A.Ph. Reynaert from the physical laboratory of the University of Amsterdam. The method of atomic absorption was used in all cases. Our values for the electrical resistivity per at.% Cr of Pt-Cr alloys are smaller than the value of $6.7 \mu\Omega$ cm/at.% Cr given by Nagasawa¹⁵⁷).

The values of $\Delta\rho/c$ for Pd-Cr alloys in table IV.2 show somewhat more variation than for the Pt-Cr alloys in table IV.1, both when nominal and when analysed concentrations are used. The nominal and analysed Cr-concentrations are again in reasonably good agreement however. The resistivities per at.% Cr

of Pd-0.25 at.% Cr (b) and Pd-0.50 at.% Cr are rather small. This may be due to an accidentally high residual resistivity of the pure Pd-wire, since the positive T^2 -term in the resistivity of Pd-W2231 is in good agreement with the same term of Pd-S8750. Also the T^2 -terms of Pd-0.25 at.% Cr (b) and Pd-0.50 at.% Cr fit in reasonably well with the other alloys (fig. IV.7 and table IV. 4). The wire Pd-0.25 at.% Cr (a) was annealed at 800°C and measured from 0.1 to 4 K (fig. IV. 5).

For Pd-Cr our values of $\Delta \rho/c$ are in good agreement with the number of $4.6 \mu\Omega \text{ cm/at.}\% \text{ Cr}$ given by Nagasawa¹⁵⁷).

IV.2.2. Resistance measurements

Specimen wires were mounted in longitudinal grooves on the outer surface of a quartz-tube of 10 cm length and 14 mm diameter, which could accommodate 5 wires. The wires were tied up and if necessary insulated by means of glass-fibre 'spaghetti' (this glass-fibre can withstand temperatures up to 600°C ; if annealing above 600°C was performed the wires were tied up after the annealing). Potential leads cut from the same wire as the specimen were spot-welded to the wire at a distance of 16 cm from each other. All current- and potential-leads were fixed at one end of the quartz tube. After mounting and annealing the quartz specimen-holder was placed in the apparatus *) which is shown in fig. IV.2. The construction is very simple. A brass vacuum-can

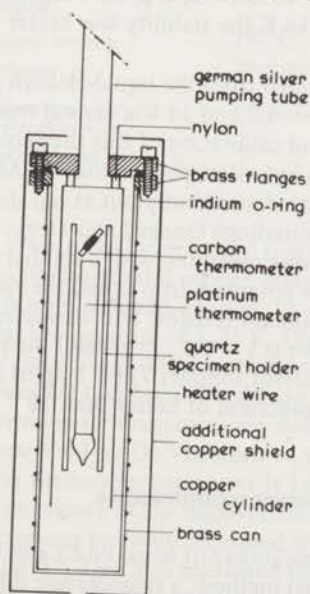


fig. IV.2 Schematic view of the apparatus. Wires have been omitted for clarity.

*) designed and built by C. van Baarle and P. Winsemius.

is sealed by means of an Indium O-ring. A heater wire is wound and glued upon the outer wall of the vacuum-can by means of Araldite. Inside the can a copper cylinder (wall thickness 0.3 mm), closed at the top and open at the bottom, is fixed to the upper flange by means of two nylon rods. The quartz specimen-holder is pushed into the copper cylinder. Knots in the glass fibre, used to fix the wires, serve as spacers. Current- and potential-leads from the measuring equipment, entering through the pumping-tube, are wound and glued upon the copper cylinder and are soldered at the bottom to the specimen-current and -potential leads. During the measurements the can and pumping-tube are filled with Helium gas. The pumping tube passes through an O-ring seal at the top of the cryostat so that the apparatus can be moved up and down. Measurements in the liquid Helium and liquid Hydrogen temperature regions were performed with the apparatus immersed in the liquid, the Helium gas providing for heat exchange. Temperatures between 4.2 K and 14 K and above 20 K were attained by pulling the apparatus above the liquid Helium or Hydrogen level. The pressure of the Helium gas (2 atm max) was used to regulate the temperature. The pumping-tube was connected to an oil-manometer. The oil-level moved between the 'plates' of a condenser (a rod, inside a cylinder), causing variations of capacitance. This change of capacitance was used to actuate a relay by means of a Fielden 'Tektor'. When the pressure of the Helium gas is low the relay directs a current through the heater wire on the brass can. When the pressure is high, a current is passed through a heater in the cooling liquid (He or H₂) and the cold gas flowing along the apparatus provides for adequate cooling. In this way a good temperature regulation was achieved. Between 4 and 14 K the stability was better than 0.005 K, above 20 K better than 0.05 K.

Temperatures were determined from the liquid-Helium and liquid-Hydrogen vapour-pressure scales. Between 4.2 and 14 K a carbon resistance thermometer was used. The manufacture and calibration of this thermometer have been described extensively by us in an earlier publication¹⁴⁶). Above 20 K a Platinum thermometer was used, calibrated and kindly put at our disposal by the thermometry group of the Kamerlingh Onnes Laboratory.

The specimen resistances were measured with a six-dial Guildline potentiometer, comparing the potential-drop across the specimen wires with the potential-drop across a standard resistor. Wire diameters were chosen such that the resistance was of order 0.1 - 1 Ω . In general the measuring current was 5 mA. We used ultra-stable current supplies *) (≈ 1 ppm) and a Keithly model 147 null detector. A relative precision of better than 10^{-5} could thus easily be achieved.

IV.2.3. Thermoelectric-power measurements

The absolute thermoelectric power of some Pd-Cr and Pt-Cr wires has been measured using the differential method: a temperature difference ΔT is created between the ends of the specimen wire; the ends of the wire are connected via superconductors to an isothermal station (e.g. the Helium bath)

*) manufactured by: 'Laboratorium voor Instrumentele Electronica', Amsterdam.

and subsequently to a Keithly 148 nanovoltmeter, which measures the thermoelectric voltage. A calibrated resistor in the thermocouple circuit is used to calibrate the reading of the nanovoltmeter. The thermopower $S = \Delta V / \Delta T$ (*). Superconductors are used as reference wires because they do not contribute to the thermopower below their transition temperature T_C . We only performed thermopower measurements below T_C , i.e. about 10 K for Nb-Ti alloy and about 16 K for Nb_3Sn .

Thermopowers were measured in a brass vacuum can, to the bottom of which an Electrovac metal-glass seal was soldered. The specimen wires were mounted upon this seal (it is essentially an 8- or 11-pole male metal 'octal'-type plug). A thick insulated vertical copper wire (2 mm dia.) was screwed to the seal. Two copper rods were horizontally connected to this wire with Johnson and

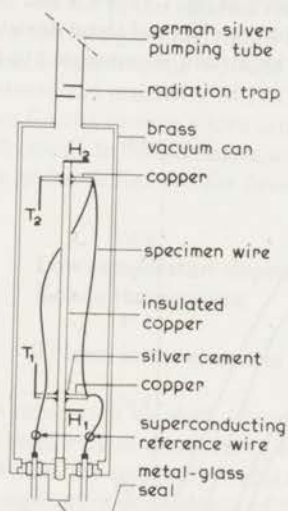


fig. IV.3 Apparatus for thermopower measurements. H_1 and H_2 are heaters, T_1 and T_2 are thermometers.

Matthey silver cement. This provided for good thermal contact while maintaining electrical insulation. To the horizontal copper rods, the specimen wire, reference wires and thermometers were soldered. During the measurements the Helium bath is kept at its lowest temperature of 1.25 K. Higher specimen temperatures are attained with H_1 . Temperature differences are applied by means of H_2 . The carbon thermometers are home-made and have been described elsewhere by the author¹⁴⁶. The thermometer resistances are measured in a double wheatstone-bridge as described by De Vroomen et al.¹⁵⁸.

A typical value of the thermoelectric power is $1 \mu V/K$. With a ΔT of 0.1 K, $\Delta V = 10^{-7}$ Volt. The noise figure of the nanovoltmeter is about 10^{-9} V so that the thermoelectric voltage can be easily measured with 1% precision.

In the apparatus of fig. IV.3 we also measured the resistivity of the pure Cu and Cu-50 ppm Fe up to 16.5 K as mentioned in section II.5. The specimen holder was mounted with a screw on the bottom seal and a heater and a carbon thermometer were used to regulate and measure the temperature.

*) The sign of S is determined from $S = - \text{grad } V / \text{grad } T$.

IV.2.4. Specific heat measurements

The specific-heat values to be discussed in this chapter were put at our disposal by B.M. Boerstael and J.J. Zwart. The equipment and experimental procedure have been described by Boerstael^{131, 132}).

IV.3. Electrical resistivity of Pd-Cr and Pt-Cr up to room-temperature

The electrical resistivity of some dilute Pd-Cr and Pt-Cr alloys is shown in fig. IV.4. In the curves of the three most dilute alloys a local maximum is observed at about 40 K. This maximum is due to deviations from Matthiessen's rule, i.e. the lattice contribution to the electrical resistivity of the alloy is larger than the lattice contribution to the resistivity of the pure host. The low-temperature side of this effect has been shown in fig. I.3 for Cu and Cu-Sn alloys. If the impurity-concentration is increased the effect of these deviations from Matthiessen's rule becomes relatively less important as compared to the temperature-dependent Cr-resistivity.

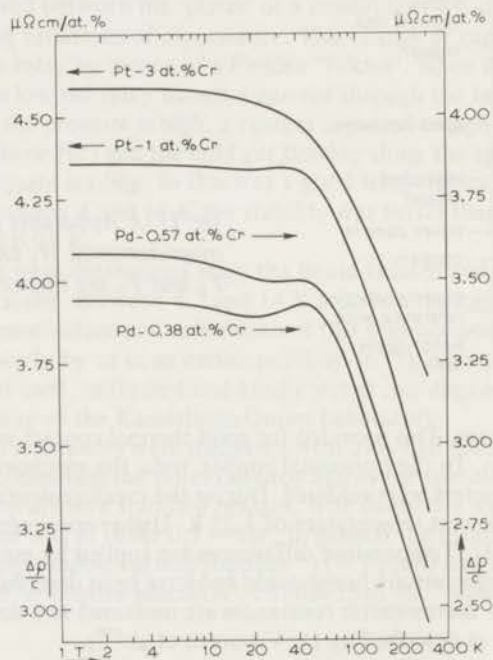


fig. IV.4 Electrical resistivity of some Pd-Cr and Pt-Cr alloys. For convenience of plotting $\Delta\rho$ was divided by the nominal concentration for Pt-Cr and by the analysed concentration for Pd-Cr alloys.

Deviations from Matthiessen's rule in copper-alloys show a maximum at about 50 K^{42, 159}), comparable to the temperature of the maxima seen in fig. IV.4. The reason may be, that the Debye-temperatures of Pd and Cu are of

the same order of magnitude. At low temperatures, when the lattice resistivity is small, deviations from Matthiessen's rule can be neglected. At room-temperature, far above the maximum, these deviations are probably small. Thus, the decrease of the resistivity from $T=0$ to room-temperature as shown in fig. IV.4 is probably quantitatively correct. Comparing the curves of fig. IV.4 with the computed curves of fig. I.7 and fig. III.1 and with Loram's universal curve for Cu-Au-Fe⁶⁵), we may expect that the Cr contribution to the resistivity is still strongly temperature-dependent even at the melting temperature of the host. Furthermore, we may estimate that the Kondo-temperature of both Pd-Cr and Pt-Cr is of order 300 K (see further section IV.4).

From the results of Kume⁵⁷) we deduce that $\rho(0\text{ K}) - \rho(300\text{ K}) \approx 2.3\ \mu\Omega$ cm/at.% for Au-V. This is twice the value for Pd-Cr and Pt-Cr. It is difficult to compare Au-V with Pd-Cr and Pt-Cr however. Although $T_K=300\text{ K}$ is estimated for Au-V, the residual resistivity is $15\ \mu\Omega$ cm/at. % V so that resonance-scattering is much more important than in Pd-Cr and Pt-Cr.

A remark regarding the work of Nagasawa¹⁵⁷) is in order. This author has also measured the resistivity of Pt-Cr alloys (0.5 - 3.5 at. % Cr) and finds that $\Delta\rho$ -values for the various alloys can be scaled to a single curve from 1 - 80 K. This is obviously in disagreement with fig. IV.4. Nagasawa does not mention if or how he has accounted for deviations from Matthiessen's rule.

IV.4. Low-temperature dependence of transport properties; the Kondo-temperature

IV.4.1. T^2 term in the electrical resistivity

In this subsection we shall discuss the temperature-dependence of the electrical resistivity of dilute Pd-Cr and Pt-Cr below 10 K, i.e. the region in fig. IV.4 where the resistivity seems to be nearly constant.

The temperature dependence of the resistivity below 4 K is shown in fig. IV.5. We note that the T^2 -law is well obeyed. No curvatures such as seen for Cu-Fe in fig. II.4 or for Au-V in fig. II.14 have to be accounted for. Admittedly the temperature-region is limited: 1.2-4.2 K. Above 4.2 K the lattice resistivity of Pd and Pt increases rapidly with temperature and, moreover, deviations from Matthiessen's rule occur (section IV.4.3) so that a T^2 -term in the resistivity above 4.2 K is not easily demonstrated. We therefore measured one wire from 0.1 - 4.2 K as shown in fig. IV.5. The T^2 -law is clearly valid down to very low temperatures.

It is seen in fig. IV.5 that the slope of the lines increases with Cr-concentration for both Pd-Cr and Pt-Cr. Thus Cr-Cr interactions must occur, otherwise all lines of fig. IV.5 should be parallel within the relative accuracy of the analysed Cr-concentration. Errors in the Cr-concentration cannot account for a change of the slope by a factor of nearly two.

Interaction effects will be discussed in more detail in section IV.4.3. At the present stage only a few remarks will be made, with regard to other 'Kondo-alloys'. In the case of Cu-Fe we had to subtract a small $\ln T$ -term, apparently caused by interacting, nearly magnetic Fe-pairs, to obtain the T^2 -term in the resistivity. In the case of Au-V we observed for only one specimen that the

experimental points did not deviate appreciably from a straight line on a plot of $\Delta\rho$ vs. T^2 (fig. II.14). In the case of Au-Co the Co-atoms apparently interact so strongly with each other, that it has not been possible to infer a T^2 -dependence of the resistivity-contribution by isolated Co-atoms from the experimental results¹⁶⁰). In contrast to these systems, the resistivity of Pd-Cr and Pt-Cr alloys varies as T^2 for a fairly wide range of Cr-concentrations. We do not understand the difference. It should be noted that Fe is not very well soluble in Cu and neither is Co in Au. On the other hand Cr is well soluble in Pd and Pt, but V is also well soluble in Au.

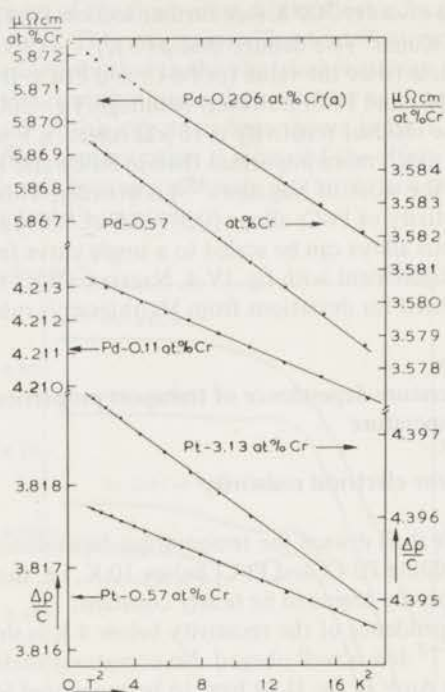


fig. IV.5 Electrical resistivity per at.% Cr versus T^2 of some Pd-Cr and Pt-Cr alloys. Analysed Cr-concentrations have been used, see table IV.1 and table IV.2. The wire of the alloy Pd-0.206 at.% Cr (a) has been annealed at 850 °C during 3 hours which might explain the high value of the resistivity (table IV.2).

We shall see in section IV.4.3 that although $\Delta\rho \sim -T^2$ at low Cr-concentrations, deviations from this simple behaviour occur at higher Cr-concentrations. These are caused by Cr-Cr interactions, which tend to make the impurity 'more magnetic', just as we saw for Cu-Fe and Au-V in chapter II.

According to Nagasawa¹⁵⁷) the resistivity of Pd-Cr dilute alloys would vary as T^2 up to $T^2 = 120 \text{ K}^2$ and of Pt-Cr alloys up to $T^2 = 250 \text{ K}^2$. We shall see in section IV.4.3 that this cannot be true if the resistivity of the pure host is simply subtracted from the resistivity of the alloys, as was apparently done by Nagasawa.

IV.4.2. Thermoelectric power of Pd-Cr and Pt-Cr at low temperatures

If the electrical resistivity varies as T^2 one may expect the thermoelectric power to be proportional to T in the same temperature region. If we apply expression (II.11 c):

$$S(T) = \frac{k_B}{e} \frac{\sin 2\delta}{A + \cos 2\delta} \frac{2\pi^2}{3} \frac{T}{\Delta} \quad (\text{II.11 c})$$

this is immediately evident. But even if this expression were not directly applicable to complicated hosts as Pd and Pt, it is physically reasonable that the thermopower should be proportional to T if $\Delta\rho \sim -T^2$.

We have measured the thermoelectric power of pure Pd and some Pd-Cr alloys and of one Pt-Cr alloy. Results are shown in fig. IV.6. The data of the two most concentrated alloys of fig. IV.6a have not been included in table IV.2.

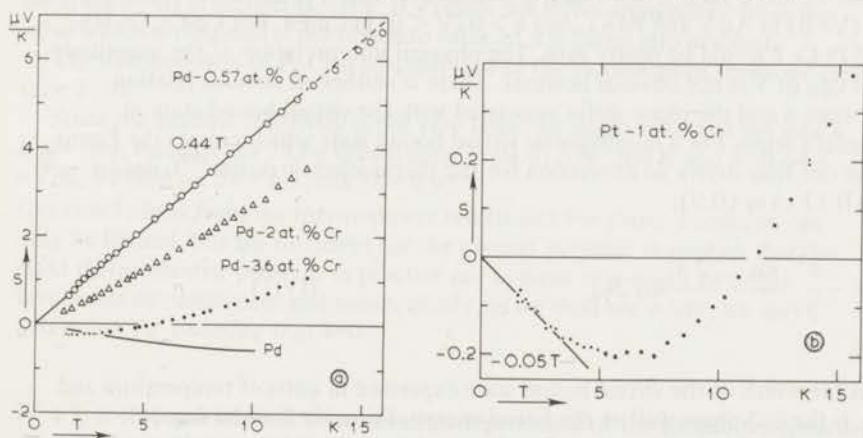


fig. IV.6 a Thermoelectric power of pure Pd and some Pd-Cr alloys.
b Thermoelectric power of a Pt-Cr alloy.

Resistivity and susceptibility data of these alloys have been published earlier⁸³). Because of interaction effects the electrical resistivity does not vary as T^2 below 4 K and neither is the thermopower proportional to T .

The thermopower of Pd-0.57 at.% Cr is well proportional to T and our value $S=0.44 T \mu\text{V/K}$ is nearly the same as observed by Gainon and Siero¹⁵⁶) on a Pd-1 at.% Cr alloy. Comparison with other, nonmagnetic solutes such as V, Ti¹⁵⁶) or Ag¹⁶¹) shows that the thermopower of Pd-Cr is indeed anomalously large and is apparently related to the 'Kondo-effect' in the electrical resistivity. In contrast to Pd-Cr, the thermopower of Pt-Cr has a 'normal' value, i.e. comparable to Pt-Au for example¹⁶¹). The electrical resistivity of Pt-1 at.% Cr varies as T^2 (fig. IV.5) and the concentration of 1 at.% Cr is large enough for Cr to dominate the conduction-electron scattering in the Pt-Cr alloy. Thus the negative term in the thermopower of Pt-Cr, proportional to T , is apparently due to electron-impurity scattering. The positive contribution, which becomes important above 5 K, is the phonon-drag thermopower.

A discussion of the magnitude of the thermopower is of some importance with respect to the estimate of T_K . We shall refer to expression (II.11 c) in this discussion. Although it worked quite well in the case of Cu-Fe (Chapters II, III) we cannot provide sound reasons why this expression should also be appropriate to Pd-Cr and Pt-Cr. However, if impurity-scattering dominates and if the electron-transport properties are determined mainly by the host sp-band, the use of (II.11 c) as a phenomenological expression, relating S and ρ (II.11 a and b) may be justified. Besides, as we shall see below, we have no other useful expression for S at our disposal.

The sign of the thermoelectric power in (II.11.c) is determined by the sign of δ . In chapter III we have seen that $\delta = -\pi\rho_1 V$, where V is the one-electron potential (in the s-d exchange model). It is generally observed that the thermoelectric power is positive when the virtual d-state is less than half filled (Au-V) and negative when the d-state is more than half filled (Cu-Fe, Au-Co). If the virtual d-state is half filled, S is small (Cu-Mn, Au-Mn). Thus δ would be <0 ($V > 0$) in Au-V and Pd-Cr, and $\delta > 0$ ($V < 0$) in Cu-Fe. For Cu-Cr, Cu-Mn and Pt-Cr δ would be nearly zero. The physical interpretation of the magnitude and sign of V is not obvious however. There is neither an obvious relation between δ and the phase-shifts associated with the virtual bound state in Friedel's sense. For a nonmagnetic virtual bound state which crosses the Fermi-level one may derive an expression for the thermoelectric power¹⁶³, similar to (II.11 c) or (II.9):

$$S = -\frac{\pi^2}{3} \frac{k_B}{e} \frac{2T}{\Gamma} \sin 2\eta_2 \quad (\text{IV.1})$$

Γ is the width of the virtual bound state expressed in units of temperature and η_2 is the $\ell=2$ phase-shift at the Fermi-energy. From the Friedel sum-rule it follows that $Z=10\eta_2/\pi$ where Z is the number of the electronic charges in the screening cloud about the impurity. If Z were < 5 for impurities to the left of Mn and $Z > 5$ to the right of Mn then we had accounted for the sign of S . But Γ would have to be unreasonably small to account for the magnitude of S (see below). This problem might be solved by a spinfluctuation theory⁷⁵) but such a theory has not yet been developed far enough to be applicable to systems like Cu-Fe or Pd-Cr. Moreover we cannot relate η_2 with δ in a physically reasonable way. We shall therefore take a pragmatic point of view and shall try to evaluate δ phenomenologically, in order to learn if the value of δ is important to our evaluation of T_K (section IV.4.3).

From the way in which A was introduced in section II.5.2. we know that $A \geq 1$, thus the maximum value of the thermopower for a given value of δ and Δ is

$$S(T) = \frac{k_B}{e} \frac{\sin 2\delta}{1 + \cos 2\delta} \frac{2\pi^2}{3} \frac{T}{\Delta} = \frac{k_B}{e} \frac{2\pi^2}{3} \frac{T}{\Delta} \frac{1}{\text{tg} \delta} \quad (\text{II.9})$$

Since we are dealing with resistance minima, $\cos 2\delta$ should be positive (see below, II.11 b) thus $-\pi/2 < 2\delta < +\pi/2$. The maximum value for the thermopower is therefore $\pm (k_B/e)(2\pi^2/3)T/\Delta = 567 T/\Delta \mu\text{V/K}$. If we

substitute $\Delta \approx 20$ K for Cu-Fe this would give $-S=28$ T μ V/K which is much higher than the observed value of 3 T μ V/K. If we substitute $\Delta \approx 300$ K for Au-V we have $S=1.9$ T μ V/K. Kume observed $S=0.09$ T μ V/K for Au-0.1 at. % V¹⁶². If we substitute $\Delta \approx 200$ K for Pd-Cr (our earlier estimate⁸³), see also section IV.4.3) we find $S=2.8$ T μ V/K, as compared to the experimental value of 0.44 T μ V/K. It thus appears that the observed thermopower values are much smaller than the maximum possible values as obtained from (II.9). It should be emphasized, however, that these maximum values correspond to $\cos 2\delta = 0$, i.e. no resistance anomaly. A giant thermopower not associated with a resistance anomaly has never been observed. So in practise we have $|\sin 2\delta| < 1$. Moreover Cu-Fe and Au-V have a high residual resistivity, i.e. $A > 1$. From our analysis of Cu-Fe transport properties in section II.5.2 we obtained $A=5.27$ and $2\delta = 0.649$ thus $\cos 2\delta=0.8$. Consequently the value of T_K obtained from Nagaoka's expression (i.e. assuming $\delta=0$) in section II.6 (fig. II.7) does not differ appreciably from the value which is obtained if the non-zero value of δ is taken into account.

The thermopower of Pt-Cr is so small that in the picture given above we can take $\delta=0$.

Since the residual resistivity is not very large, we might take $A=1$ for Pd-Cr. If we then estimate $\sin 2\delta$ by substituting in (II.9) $\Delta \approx 200$ K and $S=0.44$ T μ V/K, we find $\sin 2\delta=0.3$, $\cos 2\delta=0.95$.

Our conclusions from the thermopower results and the above discussion can only be limited, but are sufficient for the present purpose: it appears that the giant thermoelectric power is in practice not as giant as it might be under favourable circumstances and consequently, as we shall see below, we may determine T_K assuming that $\delta=0$.

IV.4.3. Magnitude and concentration-dependence of the Kondo-temperature as determined from the low-temperature resistivity

We shall define a Kondo-temperature for Pd-Cr and Pt-Cr in the same way as we did for Cu-Fe in section II.6. We have two reasons to do so. The first is that we do not know a better method. The second is that Nagaoka's expressions appeared to describe very well the low-temperature properties of Au-V and Cu-Fe. We want to see if and to which extent Nagaoka's expressions may also describe the low-temperature properties of Pd-Cr and Pt-Cr. In particular we want to investigate the concentration-dependence of T_K , which appeared already from fig. IV.5.

We recall two expressions from chapter II:

$$\rho(T=0) = c\rho_{\text{u}}(A + \cos 2\delta)/2 \quad (\text{II.11 a})$$

$$\frac{d\rho}{d(T^2)} = -c\rho_{\text{u}} \cos 2\delta \cdot \frac{\pi^2 T^2}{3 \Delta^2} \quad (\text{II.11 b})$$

We substituted $\text{Spin}=\frac{1}{2}$ in (II.11 a). ρ_{u} is the unitarity limit for the resistivity i.e. 3.8 $\mu\Omega$ cm/at.% for an impurity in copper (free-electron value). In section

IV.4.2 we inferred from the absolute value of the thermopower that δ should be rather small. Since the residual resistivity of both Pd-Cr and Pt-Cr is of order $4 \mu\Omega \text{ cm/at.}\%$ we shall assume $A=1$. Thus $\rho(T=0) \approx c \rho_U$. In order to evaluate Δ (or T_K) from (II.11 b) we have to adopt a value for ρ_U . This is a difficult problem. We have the expression

$$\rho_U = \frac{4\pi c \hbar}{e^2 k_F} \quad (\text{IV.2})$$

for a free-electron metal. For a one-band conductor like copper the use of this expression may have provided a good approximation for ρ_U . The Fermi-surface of Pd and Pt is much more complicated than that of Cu however. In addition to a closed sp-electron surface, Pd and Pt have a closed and an open surface of d-electrons. All may contribute to the electron transport properties. The d-electrons are much heavier than the sp-electrons, however. Thus, if quantitative estimates for transport properties in Pd- or Pt-alloys are made, it is sometimes assumed that all the current is carried by the sp-electrons, which are considered to be free^{148, 161}).

Palladium has 0.364 sp-electrons per atom¹⁶⁴). If we assume that these electrons are free we find $\rho_U = 5.7 \mu\Omega \text{ cm/at.}\%$ impurity using (IV.2). Platinum has 0.426 sp-electrons per atom¹⁶⁵). Again using (IV.2) and the free-electron model we find $\rho_U = 5.5 \mu\Omega \text{ cm/at.}\%$ impurity. Both values for ρ_U are larger than the residual resistivity of Cr in Pd and Pt. But the sp-electrons of Pd and Pt are not free. The effective masses are considerably larger than 1. In particular, the sp- and d-bands of Pt are severely hybridized and the Fermi-velocities of the sp-electrons of Pt are smaller than those of Pd and about a factor of 2 smaller than the free-electron value¹⁶⁶). Consequently the d-electrons of Pt, since they are more sp-like, have a higher Fermi-velocity than the d-electrons of Pd. Actually it is possible, both theoretically and experimentally, to determine the Fermi-velocities. But even if we had them all available and if we were able to evaluate ρ_U correctly, we still had to consider the problem of the small residual resistivity of Pd-Cr and Pt-Cr. In alloys of a noble metal with a transition metal the residual resistivity (far below T_K) is quite large: $15 \mu\Omega \text{ cm/at.}\%$ V in Au-V, $12 \mu\Omega \text{ cm/at.}\%$ Fe in Cu-Fe, $20 \mu\Omega \text{ cm/at.}\%$ Cr in Cu-Cr¹¹⁸). But large residual resistivities are also observed when the host is a transition metal. For instance, about $7 \mu\Omega \text{ cm/at.}\%$ Co has been found for Mo-Co⁸⁰) and $12 \mu\Omega \text{ cm/at.}\%$ Ce for Y-Ce⁸¹). On the other hand Sarachik¹⁸) observed a distinct, but rather small variation ($\approx 2 \mu\Omega \text{ cm/at.}\%$) of the residual resistivity of Fe dissolved in Nb-Mo and Mo-Re host-alloys. The maximum residual resistivity observed was smaller than $4 \mu\Omega \text{ cm/at.}\%$ Fe.

The residual resistivity of V and Mo in Pd and Pt, which elements do not cause resistance anomalies like Cr (see however also the Addendum) is of the same order of magnitude as the residual resistivity of Cr: $4-6 \mu\Omega \text{ cm/at.}\%$. The presence of d-electrons at the Fermi-energy of the host apparently complicates the behaviour of the residual resistivity of transition-metal impurities and the occurrence of a resistance minimum is not as clearly associated with a scattering resonance as with noble-metal hosts.

From fig. IV.4 we may estimate that the total decrease in resistivity from

$T \ll T_K$ to $T \gg T_K$ will be at least $2\mu\Omega$ cm/at. % Cr for both Pd-Cr and Pt-Cr. Thus for ρ_U we should take at least $2\mu\Omega$ cm/at. % . Since any value which we adopt for ρ_U is apparently arbitrary, we shall take the average value of the residual resistivity, as obtained from tables IV.1 and IV.2. These values are anyway close to the value of $3.8\mu\Omega$ cm/at. % used for Copper in Chapter II. We thus assume $\rho_U = 3.8\mu\Omega$ cm/at. % Cr for Pd-Cr and $\rho_U = 4.2\mu\Omega$ cm/at. % Cr for Pt-Cr. The Kondo temperature is then obtained from (II.11 b) with $\cos 2\delta = 1$ and $T_K = 1.14\Delta$. In view of all uncertainties we could equally well take $T_K = \Delta$, but we shall try to be consistent with the analysis in section II.6.

We have analysed our resistivity data on both Pt-Cr and Pd-Cr using the expression

$$\rho(T) = \rho(T=0) + AT^2 + BT^5 \quad (IV.3)$$

It appeared from our experimental results that the phonon-term in the electrical resistivity of Pt and Pd is proportional to T^5 up to 10 K. Above 10 K the resistivity increases less rapidly with temperature. We thus made least-squares fits of our data to (IV.3) from 1.2 – 10 K. Relevant figures are given in table IV.3 for Pt-Cr and in table IV.4 for Pd-Cr. It should be noted that the host-resistivity was not subtracted.

As can be seen from the values of the r.m.s. deviation, the representation of the data by (IV.3) is very good. The error in the resistivity measurements is of the same order of magnitude as the r.m.s. $\Delta\rho$. Only for the higher concentrations, in particular Pt-3 at. % Cr and Pd-1 at. % Cr (nominal) the r.m.s.-deviation is larger than the experimental error. This is caused by interaction effects. Above a certain Cr-concentration these become so important that a T^2 -term for the Cr-contribution to the resistivity is no longer observed (see below).

From the precision of the least-squares fits we may conclude that the Cr-contribution to the electrical resistivity is probably proportional to T^2 up to 10 K so that the next term (T^4) is still rather small at 10 K. This would be in agreement with our observations on Cu-Fe in Chapter II. We have seen that the T^2 -term of Cu-Fe is valid up to about 1 K. From tables IV.3 and IV.4 we conclude that T_K for Pd-Cr and Pt-Cr is about a factor of 10 higher than T_K of Cu-Fe. Thus, if the T^2 -dependence were valid up to the same value of T/T_K for any value of T_K , it would be valid up to about 10 K for Pd-Cr and Pt-Cr.

The coefficient of the lattice resistivity is seen to increase with the host-resistivity. This is probably the same type of deviation from Matthiessen's rule as was shown for Cu and Cu-Sn alloys in fig. I.3. The increase of B is so large that a substantial T^5 -term remains if the host resistivity is subtracted from the resistivity of the alloy. Thus $\rho - \rho_{\text{host}}$ certainly does not vary as T^2 up to 10 K for Pd-Cr and up to 15 K for Pt-Cr, as was suggested by Nagasawa¹⁵⁷).

The value of $|\Delta A/c|$ increases rapidly with Cr-concentration for both Pd-Cr and Pt-Cr. We have used the nominal as well as the analysed Cr-concentrations, in order to demonstrate that errors in the concentrations are certainly not the cause. We have plotted the T_K -values from tables IV.3

Table IV.3

Analysis of Pt-Cr resistivity data with expressions (IV.3) and (II.11b). A fit was made to about 20 points from 1.2 – 10 K. One Pt – 1 Cr alloy was only measured from 1.2 – 4.2 K. $\Delta A = A - A_{Pt}$

Alloy at. % Cr nominal	$\rho(T=0)$ $\mu\Omega\text{cm}$	A $\mu\Omega\text{cm}/\text{K}^2$	B $\mu\Omega\text{cm}/\text{K}^5$	r.m.s. $\Delta\rho$ $\mu\Omega\text{cm}$	$\Delta A/c_{\text{nom.}}$ $\mu\Omega\text{cm}/\text{at. \% K}^2$	T_K (K)	$\Delta A/c_{\text{anal.}}$ $\mu\Omega\text{cm}/\text{at. \% K}^2$	T_K (K)
Pt-S3389	0.012466	1.45×10^{-5}	1.80×10^{-8}	8×10^{-6}	—	—	—	—
Pt-0.5 Cr	2.18865	-3.65×10^{-5}	2.60×10^{-8}	1.1×10^{-5}	-1.02×10^{-4}	420	-0.89×10^{-4}	448
Pt-1 Cr	4.41772	-9.8×10^{-5}	—	—	-1.13×10^{-4}	400	-1.00×10^{-4}	423
Pt-1 Cr	4.39487	-9.53×10^{-5}	2.60×10^{-8}	1.7×10^{-5}	-1.10×10^{-4}	404	-0.97×10^{-4}	430
Pt-S8713	0.03701	1.35×10^{-5}	1.77×10^{-8}	1.2×10^{-5}	—	—	—	—
Pt-0.75Cr	3.27854	-6.31×10^{-5}	2.45×10^{-8}	9×10^{-6}	-1.02×10^{-4}	419	-0.86×10^{-4}	457
Pt-1.5 Cr	6.78137	-16.72×10^{-5}	2.86×10^{-8}	3.5×10^{-5}	-1.20×10^{-4}	386	-1.14×10^{-4}	396
Pt-3 Cr	13.8015	-43.14×10^{-5}	4.54×10^{-8}	1.4×10^{-4}	-1.48×10^{-4}	348	-1.42×10^{-4}	355

It has been assumed, that the T^2 -term of the host-resistivity does not change upon the addition of Cr. Actually, this term decreases, but the influence on the value of $\Delta A/c$ can be neglected. See also the Addendum to this chapter.

Table IV.4

Analysis of Pd-Cr resistivity data with expressions (IV.3) and (II.11b). A fit was made to about 20 points from 1.2 – 10 K. Pd-0.25 (Cr) was measured from 0.1 – 4.2 K. $\Delta A = A - A_{Pd}$.

Alloy at. % Cr nominal	$\rho(T=0)$ $\mu\Omega\text{cm}$	A $\mu\Omega\text{cm}/\text{K}^2$	B $\mu\Omega\text{cm}/\text{K}^5$	r.m.s. $\Delta\rho$ $\mu\Omega\text{cm}$	$\Delta A/c_{\text{nom.}}$ $\mu\Omega\text{cm}/\text{at. \% K}^2$	T_K (K)	$\Delta A/c_{\text{anal.}}$ $\mu\Omega\text{cm}/\text{at. \% K}^2$	T_K (K)
Pd-S8750	0.067920	2.68×10^{-5}	1.34×10^{-8}	5.9×10^{-6}	—	—	—	—
Pd-0.1 Cr	0.531410	0.28×10^{-5}	1.69×10^{-8}	4.4×10^{-6}	-2.41×10^{-4}	260	-2.19×10^{-4}	273
Pd-0.2 Cr	0.849919	-2.72×10^{-5}	2.18×10^{-8}	9.5×10^{-6}	-2.70×10^{-4}	245	-3.00×10^{-4}	233
Pd-0.4 Cr	1.37659	-8.16×10^{-5}	2.77×10^{-8}	2.9×10^{-5}	-2.71×10^{-4}	245	-2.85×10^{-4}	239
Pd-0.6 Cr	2.11146	-17.44×10^{-5}	4.24×10^{-8}	7.6×10^{-5}	-3.35×10^{-4}	220	-3.53×10^{-4}	215
Pd-W2231	0.52518	2.61×10^{-5}	1.41×10^{-8}	1.1×10^{-5}	—	—	—	—
Pd-0.25Cr a	1.73490	-4.24×10^{-5}	—	—	-2.74×10^{-4}	244	-3.33×10^{-4}	221
Pd-0.25Cr b	0.889697	-2.75×10^{-5}	2.09×10^{-8}	8.6×10^{-6}	-2.14×10^{-4}	275	-2.60×10^{-4}	250
Pd-0.5 Cr	1.79826	-10.52×10^{-5}	3.08×10^{-8}	5.4×10^{-5}	-2.62×10^{-4}	249	-3.18×10^{-4}	226
Pd-1 Cr	4.1841	-49.35×10^{-5}	10.9×10^{-8}	3.4×10^{-4}	-5.20×10^{-4}	177	-6.04×10^{-4}	164

It has been assumed, that the T^2 -term of the host-resistivity does not change upon the addition of Cr. Actually, this term decreases, but the influence on the value of $\Delta A/c$ can be neglected. See also the Addendum to this chapter.

and IV.4 versus Cr-concentration in fig. IV.7. Note the similarity with fig. II.7 for Cu-Fe. There is one important difference however. In the case of Cu-Fe we had to subtract a $\ln T$ -term from the resistivity, in order to obtain the T^2 -term, from which T_K was determined. In the present case the resistivity varies as T^2 for all alloys of table IV.3 and IV.4 and no extra term like $\ln T$ has to be accounted for. Again T_K decreases with increasing impurity-concentration. We consider this as a support for the analysis of section II.6. Again we want to compare the experimental results with Nagaoka's expression, which we recall

$$\Delta = \Delta_0 - \frac{c}{2\pi\rho_1} \quad (\text{II.13})$$

where c is the concentration of impurities, ρ_1 is the electronic density of states per atom per spin-direction, $T_K = 1.14 \Delta$. We have discussed this expression in section II.6. We want to repeat only that although Nagaoka's calculation may be incorrect, (II.13) should have a meaning since it appears to be physically related to the uncertainty-principle. The latter statement is

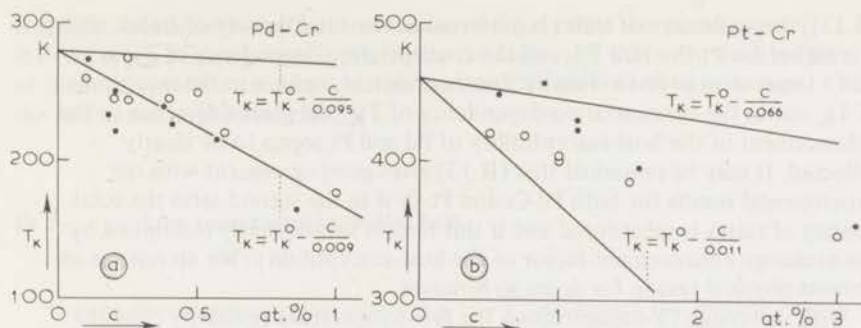


fig. IV.7 Kondo-temperatures for Pd-Cr and Pt-Cr as listed in tables IV.3 and IV.4, plotted versus Cr-concentration.

o : T_K as determined from the nominal Cr-concentration.

● : T_K as determined from the analysed Cr-concentration.

The solid lines represent Nagaoka's expression (II.13) for various values of the density of states: c in at. % Cr.

a : For the upper line the total density of states as obtained from the measured electronic specific heat was used: $2\rho_1 = 3.44 \times 10^{-4}$ states per atom per Kelvin. For the lower line the calculated sp-electron density of states was used, including an enhancement factor of 1.52^{166} : $2\rho_1 = 0.327 \times 10^{-4}$ states per atom per Kelvin.

b : Upper line: total density of states $2\rho_1 = 2.40 \times 10^{-4}$ states per atom per Kelvin.

Lower line: calculated sp-electron density of states, with enhancement factor 1.52^{166} : $2\rho_1 = 0.404 \times 10^{-4}$ states per atom per Kelvin.

made with the reservation that a spin-fluctuation lifetime may be defined by $\tau_{sf} \approx h/k_B T_K$, which is not certain if the one-electron lifetime, associated with the width of the virtual impurity-state is much shorter than τ_{sf} .

It appears from fig. IV.7a that (II.13) describes very well the concentration dependence of T_K for Pd-Cr if the sp-electron density of states is chosen. This is not unreasonable if we assume that the sp-electrons carry most of the current. In the arguments provided in section II.6 to support expression (II.13) only conduction electrons played a role.

In fig. IV.7b we observe that for Pt-Cr neither the total density of states, nor the sp-density of states describes very well the concentration-dependence of T_K . The slope of the upper line is a factor of 3 too small, the slope of the lower line is a factor of 2 too large. Using the same arguments as above for Pd-Cr we might try to account for this discrepancy: the sp- and d-bands of Pt are severely hybridized, so that more d-electrons than in Pd might be involved in the conduction and scattering processes. This interpretation is very tentative, however, since our estimates of T_K are rather crude, and the validity of (II.13) is not well established theoretically. Nevertheless, as we shall see below, the values of T_K as obtained from the specific heat are in good agreement with the values in table IV.3 and IV.4. We may thus conclude that the order of magnitude of the concentration-dependence of T_K is remarkably well predicted by (II.13) for both Pd-Cr and Pt-Cr. Furthermore, if we use

(II.13), the sp-density of states is preferred to the total density of states, since it is higher for Pt than for Pd, and the concentration-dependence of T_K is in Pd-Cr larger than in Pt-Cr. Finally, for the moment, neither in the magnitude of T_K nor in the concentration-dependence of T_K , the great difference in the enhancement of the host-susceptibility of Pd and Pt seems to be clearly reflected. It may be remarked that (II.13) gives good agreement with the experimental results for both Pd-Cr and Pt-Cr if in the second term the total density of states is substituted and if this term is subsequently multiplied by the exchange enhancement-factor of the host-susceptibility. We do not see an obvious physical reason for doing so however.

With increasing Cr-concentration the low-temperature resistivity tends to deviate from the T^2 -dependence. This appeared already from the increased r.m.s. deviation for Pd-1 at.% Cr in table IV.4 and for Pt-3 at.% Cr in table IV.3. In fig. IV.8 we observe that the deviation from the T^2 -law looks similar to the behaviour of Au-V (fig. II.14). The magnetic-field dependence is

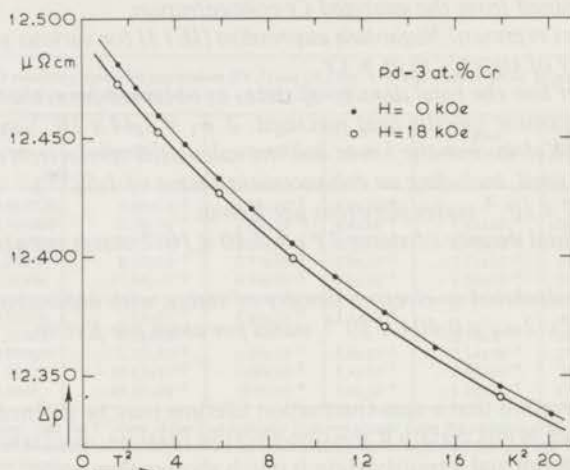


fig. IV.8 Resistivity of Pd-3 at. %Cr (2.7% analysed) versus T^2 .

different however. The negative magnetoresistance shown in fig. IV.8 is only slightly temperature-dependent, whereas for Au-1 at.% V the slope of the ρ vs T^2 curve clearly decreases in a magnetic field of 18 kOe. This difference is related to the fact that a T^2 -law for the resistivity of Pd-Cr was easily demonstrated, while in Au-V apparently particles with a low effective T_K -value are present, masking the T^2 -dependence of the resistivity caused by isolated V-Atoms. In Pd-Cr and Pt-Cr interactions tend to decrease only gradually the effective T_K -value.

It should be emphasized that the interaction-effects responsible for the curvature as exhibited in fig. IV.8 are different from the R.K.K.Y.-type interactions between 'non-compensated' magnetic moments. The latter tend to produce a maximum in the ρ vs T curve. Such a maximum also occurs in Pd-Cr and has been shown in fig. IV.1 for Pd-10 at.% Cr. What happens is that Cr-Cr interactions first create a magnetic moment on Cr-atoms and that these magnetic atoms subsequently interact with each other via the

R.K.K.Y. spindensity-oscillations. It is not unlikely that the mechanism of the two types of interaction is essentially the same, and that only the life-time of the local spinfluctuations, which is increased by the interactions, causes the difference in physical effects.

IV.5. Low temperature specific heat

In the concentration-region where $\Delta\rho \sim -T^2$ we expect the specific-heat contribution of Cr in Pd and Pt to be proportional to T . In order to investigate this the specific heat of one Pt-Cr alloy and three Pd-Cr alloys was measured. The results are shown in fig. IV.9. Only for Pd-0.43 at.% Cr the impurity specific heat is proportional to the temperature. We might also expect the specific heat of Pd-0.88 at.% Cr to be proportional to T . Although the r.m.s. deviation (table IV.4) for the analysis of the resistivity of Pd-1 at.% Cr (0.86 at.% analysed) is larger than the error in the experimental results, we did not observe appreciable deviations from the T^2 -law below 4 K. Only for Pd-1.5 at.% Cr are interaction effects expected to modify appreciably the temperature-dependence of the impurity specific heat. Just as in the case of Au-V we suggest that the Debije-temperature of Pd and Pt increases upon the addition of Cr. The Pd-atom is a factor of two, Pt a factor of four heavier than Cr. The assumption of an increasing Debije-temperature is supported by the fact that the points of $\Delta C/T$ for both Pd-0.88 at.% Cr and Pt-0.91 at.% Cr can be represented by a parabola within the estimated experimental error ($\pm 0.5\%$ of the total specific heat). Since $T_K > 100$ K, we do not expect a T^3 -term in the impurity-contribution to the specific heat to be important below 10 K. Measurements of the specific heat of Pd-V and Pt-V may provide a check to the assumed increase of the Debije-temperature. Such measurements were not performed. The specific heat of Pd-(Mo, W) and Pt-(Mo, W) may indicate how much the electronic specific heat of Pd and Pt is affected by impurities with the same valency as Cr, which do not cause a 'Kondo-effect'. Such measurements were neither performed. We shall first assume that the electronic specific heat of the host is not affected.

We shall again use Nagaoka's expression (I.17) to determine T_K from the impurity-contribution to the specific-heat:

$$\Delta C = \frac{2\pi}{3} \frac{T}{\Delta} \quad (\text{I.17})$$

per impurity, with $T_K = 1.14 \Delta$. For Pd-0.43 at.% Cr, with $\Delta C = 0.42$ T mJ/mole K we find $T_K = 200$ K and for Pt-0.91 at.% Cr, with $\Delta C = 0.52$ T mJ/mole K we find $T_K = 350$ K. Just as for Cu-Fe and Au-V (Chapter II) these numbers are in very good agreement with the T_K -values determined from the electrical resistivity (fig. IV.7).

If Cr introduces holes into the d-band when dissolved in Pd or Pt, the density of states and thus the electronic specific-heat coefficient increases. Such an increase may have contributed to the values for $\Delta C/T$ used above to determine T_K . For Pd-Rh it has been observed that $\Delta\gamma/\gamma_{Pd} = +1\%$ per

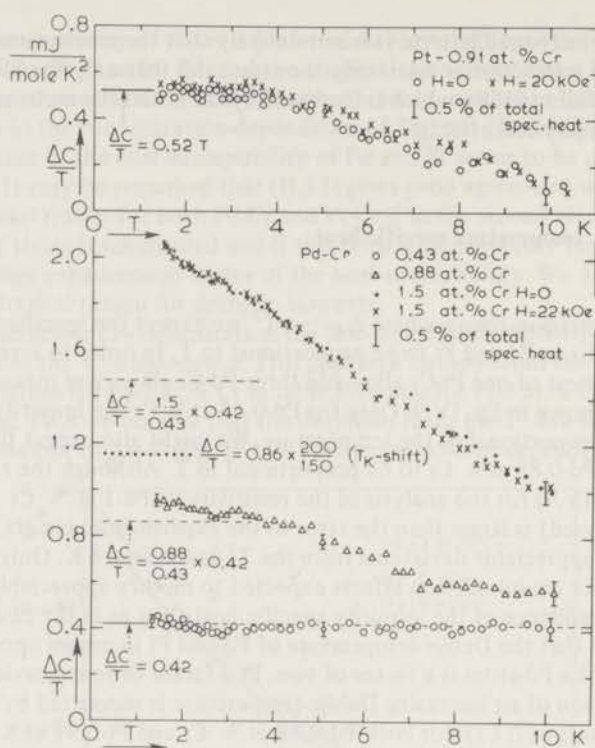


fig. IV.9 Contribution of Cr to the specific heat of Pt and Pd. The lowest concentrations have been analysed. Pd-1.5 at. % Cr and Pt-0.91 at. % Cr are nominal values. Dashed lines represent specific heat values calculated from Pd-0.43 at. % Cr assuming proportionality to concentration and temperature. The dotted line represents the specific heat of Pd-0.88 at. % Cr calculated from Pd-0.43 at. % Cr assuming a T_K -shift of 50 K according to fig. IV.7 a. Note that a magnetic field of 20 kOe has no measurable influence on the specific heat. The alloys were prepared by induction melting in Al_2O_3 crucibles under Argon atmosphere. In general they were melted during 10-20 minutes, inverted and remelted. They were annealed during 48 hours in vacuum at $1200^\circ C$ and subsequently quenched in water.

at. % Rh¹⁶⁷). Even if $\Delta\gamma/\gamma$ for Cr in Pd and Pt were +3 % per at. % Cr (not taken into account the contribution of the Kondo effect), so that we would obtain $T_K=280$ K for Pd-Cr and $T_K=535$ K for Pt-Cr, we would maintain our conclusion that T_K as determined from the specific heat is in good agreement with T_K as determined from the electrical resistivity. One may argue that Cr should not be compared with Rh, since addition of Rh causes the susceptibility of Pd to increase, whereas Cr causes it to decrease. This does not necessarily mean that Cr adds electrons to Pd however, since local enhancement effects may be important to the susceptibility of Pd-alloys. If $\Delta\gamma/\gamma$ were -3 % per at. % Cr we would obtain $T_K=155$ K for Pd-Cr and $T_K=260$ K for Pt-Cr.

The specific heat of Pd-0.88 at. % Cr below 4 K is larger than if it were

proportional to the Cr-concentration as compared to Pd-0.43 at.% Cr. This is in qualitative agreement with a decrease of T_K with increasing concentration. Quantitative agreement is poor however, as shown by the dotted line in fig. IV.9. This may be caused by errors in the analysed Cr-concentrations.

Just as in the case of Au-1% V, we believe that the temperature-dependence of $\Delta C/T$ for Pd-1.5 at.% Cr is the combined result of an increase of the Debye-temperature and Cr-Cr interactions causing an effective lowering of T_K . We cannot assign one single T_K -value to more concentrated alloys, as we did to the dilute alloys in table IV.4. Cr-atoms with a relatively low Kondo-temperature must be present, otherwise the resistivity would vary as T^2 below 4 K and we would observe a low-temperature flat region of $\Delta C/T$.

IV. 6. The magnetic susceptibility

In Chapter II the impurity-contribution to the magnetic susceptibility for $T \ll T_K$ was discussed using the empirical relation $\Delta \chi = \mu_{\text{eff}}^2/3k_B T_K$. This provided T_K -values in good agreement with values obtained from electrical resistivity and specific heat. Such a discussion is extremely difficult for Pd-Cr. The Pauli-susceptibility of pure Pd is strongly enhanced by exchange interactions between d-electrons. If impurities are dissolved in Pd these exchange interactions get reduced as appears from the decreasing susceptibility when the impurities are nonmagnetic. The positive contribution of Cr to the susceptibility of Pd, supposedly of order $\mu_{\text{eff}}^2/3k_B T_K$ at low temperatures, appears to be smaller than the negative contribution, so that the net contribution of Cr to the susceptibility of Pd is negative.

Nagasawa¹⁵⁷) relates the negative temperature-coefficient of the Pd-Cr resistivity with the decreasing susceptibility of Pd upon addition of Cr. Such a relation follows from the spinfluctuation theory by Lederer and Mills¹⁶⁸). We do not believe it is meaningful in the present case, since this theory was only developed for impurities with a negligible one-electron potential and since V or Mo also cause the susceptibility of Pd to decrease, without giving rise to a resistance minimum (see however also section IV.7).

Donzé¹⁶⁹) has attempted to evaluate that part of the contribution of Cr to the susceptibility of Pd-Cr, which is associated with the 'Kondo-effect'. He compared the susceptibility of Pd-Cr alloys with the susceptibility of Pd-Mo alloys assuming that isoelectronic solutes would affect the host in the same way. This assumption was checked by comparing the susceptibilities of Pd-1 at.% Mo and Pd-1 at.% W. These were nearly equal. The Pd-Mo data were used by Donzé to correct the Pd-Cr data for effects characteristic for the Pd-host. The susceptibility of Cr-impurities which was finally obtained qualitatively resembles that of Au-V. At low temperatures ($T < 100$ K) the susceptibility is nearly constant and around room-temperature a Curie-Weiss law is approximately obeyed with a characteristic temperature of roughly -200 K and an effective moment of about $4.9 \mu_B$. This latter value is about the same as obtained by Burger¹⁷⁰) for Cr in Pd-H (saturated with H). The susceptibility-values obtained by Donzé¹⁶⁹) were only roughly proportional to the Cr-concentration. If we take an average value of $\Delta \chi = 1 \times 10^{-6}$ e.m.u/at.% Cr gram, we may estimate T_K by means of $\Delta \chi = \mu_{\text{eff}}^2/3k_B T_K$. With $\mu_{\text{eff}} \approx 4.9 \mu_B$ we obtain $T_K \approx 280$ K

for Pd-Cr. This is in good agreement with our estimates from the resistivity and the specific heat, but may be in error by a factor of 2.

The exchange enhancement of the susceptibility of Pt is much smaller than that of Pd. If nonmagnetic impurities are dissolved in Pt the decrease of the susceptibility is also much smaller than if impurities are dissolved in Pd. Measurements by Van Dam¹³⁷⁾ show that the susceptibility of Pt-0.5 at.% Cr is slightly smaller than that of Pt above 200 K and larger below 200 K. For Pt-1 at.% Cr $\chi - \chi_{\text{Pt}}$ is positive up to room temperature. According to van Dam¹³⁷⁾ $\Delta\chi \approx 0.12 \times 10^{-6}$ e.m.u/at.% gram for Pt-Cr. This value has not been corrected for the decrease of the host-susceptibility, which is probably small. If we use again $\Delta\chi = \mu_{\text{eff}}^2/3k_{\text{B}}T_{\text{K}}$ with $\mu_{\text{eff}} \approx 4.9\mu_{\text{B}}$, we obtain $T_{\text{K}} \approx 1300$ K, about three times the value obtained from resistivity and specific heat. The value of μ_{eff} is very uncertain. If we use $\mu_{\text{eff}} = 3\mu_{\text{B}}$ like we did for Au-V in chapter II, we find $T_{\text{K}} = 490$ K. T_{K} becomes smaller if a correction for the decreasing host-susceptibility is applied.

The contribution of the susceptibility associated with the Kondo-effect in dilute Pd-Cr and Pt-Cr alloys is thus only approximately known and we can conclude only with due reserve that the same empirical relationship $\Delta\chi \approx \mu_{\text{eff}}^2/3k_{\text{B}}T_{\text{K}}$ holds as for Au-V and Cu-Fe.

We shall not discuss the susceptibility of concentrated Pd-Cr or Pt-Cr alloys. We only want to point out how the interaction effects discussed in section IV.5 appear in the susceptibility. We have shown that the effective T_{K} -value appears to decrease with increasing impurity-concentration. As long as $\Delta\rho \sim -T^2$ we may expect the susceptibility to be nearly constant at low temperatures. Above about 1 at.% Cr in Pd and 3 at.% Cr in Pt the electrical resistivity no longer varies as T^2 at low temperatures and we cannot assign one single T_{K} -value to the system*). One may either say that interactions enhance the lifetime of local spinfluctuations, or that not all impurities can have their spins compensated (in Nagaoka's sense) if the concentration increases above some critical value. A certain fraction of the impurities gets very near to being magnetic. This is reflected in the magnetic susceptibility which becomes more and more Curie-like. Thus the magnetic susceptibility of Pd-4 at.% Cr (3.5% analysed) as measured by van Dam⁸³⁾ is a factor of two smaller than of pure Pd at room-temperature, but larger than of pure Pd at liquid Helium temperatures.

IV.7. Final remarks

In section IV.1 we presumed that the host d-band would be important to the magnetic state of impurities in Pd and Pt. In section IV.4.3 we concluded that the great difference in exchange enhancement of the susceptibility between Pd and Pt does not clearly show up in the magnitude of T_{K} for Pd-Cr and Pt-Cr, nor in its concentration-dependence. We maintain the latter conclusion, adding that the macroscopic properties of Pd-Cr and Pt-Cr which we have discussed are related to each other in the same way as the properties of Au-V and Cu-Fe. Pd-Cr and Pt-Cr distinguish themselves only in their rather small residual

*) That is to say, a T_{K} -value defined in the way we did. (section II.6, IV.4.3).

resistivity as compared with dilute alloys of transition metals in non-transitional hosts.

Nagasawa¹⁵⁷) has studied the residual resistivity and the temperature-dependence of the resistivity of 0.8 at.% Cr in Pd and Pd-Rh hosts (up to 10 at.% Rh). According to Nagasawa both $\Delta \rho / c$ and $|\Delta A| / c$ (tables IV.3,4) have a maximum value at Pd-5 at.% Rh. This is the composition at which the electronic specific-heat coefficient γ and the susceptibility of the Pd-Rh system also have their maximum value. Rh introduces holes into the Pd-d-band, thus increasing the electronic density of states. One may then argue that the residual resistivity is apparently not caused by unitarity-limit exchange-scattering, since ρ_{U} is inversely proportional to the density of states, but the residual resistivity per at.% Cr in Pd-Rh (< 5 at.% Rh) is found to increase with Rh-concentration (this was pointed out by Nagasawa).

Lederer⁷³) suggests that impurity-induced s-d-band scattering may be responsible for the residual resistivity, since it is proportional to the d-band density of states. The relative variation is then not very well accounted for however. Estimated from γ , the density of state increases by 5% for 5 at.% Rh in Pd. The residual resistivity of Cr in Pd is $4.6 \mu\Omega \text{ cm/at.}\%$ Cr and in Pd-5 at.% Rh it is $9.3 \mu\Omega \text{ cm/at.}\%$ Cr¹⁵⁷). This increase by a factor of two is much larger than the increase of γ and is almost equal to the increase by a factor of 1.7 in the susceptibility⁷³).

It should be noted that Nagasawa's argument concerning ρ_{U} (IV.2) does not apply if the current is mainly carried by the sp-electrons. The sp-electron density of states decreases upon the addition of Rh to Pd in qualitative agreement with the increasing residual resistivity of Cr-impurities. Quantitative agreement is again poor.

It is clearly interesting to study the resistivity of Cr-impurities in Pd-Ag. But also the (Pd-Rh)-Cr system should be considered more carefully. Nagasawa¹⁵⁷) gives a value of $|\Delta A| / c = +5 \times 10^{-4} \mu\Omega \text{ cm/K}^2$ at.% Cr for 0.8 at.% Cr in Pd-5 at.% Rh. This is about the value which we find for Pd-1 at.% Cr (0.86% analysed). For Pd-0.8 at.% Cr Nagasawa finds $|\Delta A| / c = +4 \times 10^{-4} \mu\Omega \text{ cm/at.}\%$ Cr K^2 , which is smaller than our value (table IV.4), but larger than our limit for $c \rightarrow 0$. We therefore cannot consider the variation of $|\Delta A| / c$ with Pd-Rh host composition to be experimentally well-established until the dependence on Cr-concentration has been investigated.

The fact that we used the unitarity-limit ρ_{U} (roughly estimated) to obtain values for T_{K} does not mean that we believe the s-d exchange model should apply to Pd-Cr and Pt-Cr. We only noticed how useful Nagaoka's expressions were in the analysis of Cu-Fe and Au-V and we were able to show that in this respect Pd-Cr and Pt-Cr are no exception. If one does not believe any of the expressions which we employed, the facts remain, namely

- 1^o The impurity-contribution to the electrical resistivity of dilute Pd-Cr and Pt-Cr alloys varies as T^2 below about 10 K.
- 2^o The Cr-contribution to the specific heat of Pd and Pt is proportional to T , probably also up to about 10 K.
- 3^o In the region of temperature and concentration where the electrical resistivity contains a term AT^2 , $|\Delta A| / c$ is not constant, but increases with c .

Addendum: Another resistance minimum in Pd- and Pt-alloys

We shall briefly discuss another resistance-minimum phenomenon which we – and others – have observed in Pd- and Pt-alloys. We mentioned this already in section I.1.

In fig. IV.10b we show a detail from curve III, fig. IV.1. The 'depth' of the minimum and the temperature at which it occurs increase with Cr-concentration. Cr-moments are not the cause, since a resistance maximum occurred already in a 10 at.% alloy at 25 K, which is characteristic of magnetic ordering. Other impurities, with a low Kondo-temperature, can neither be responsible, because we did not observe any change of the resistivity in a magnetic field of 18 kOe. We presume that the origin of the resistance minimum must be sought in the band structure of the host, in particular in the fact that Pd is a component. Other – nonmagnetic – solutes in Pd (and Pt) also cause a resistance minimum.

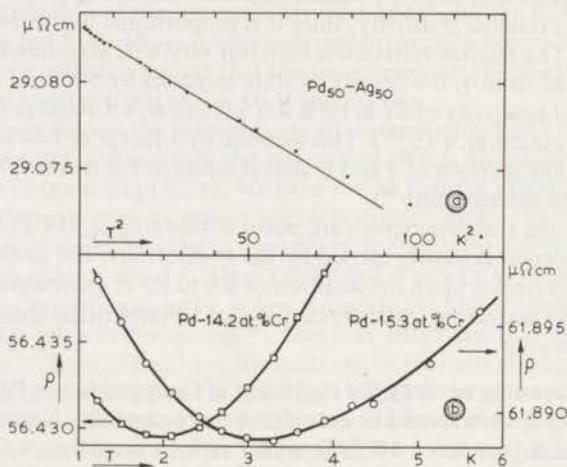


fig. IV.10 a Electrical resistivity of Pd₅₀Ag₅₀ versus T^2 (nominal composition).
b Electrical resistivity of two concentrated Pd-Cr alloys versus T (analysed concentrations).

If impurities such as V or Mo are dissolved in Pd, the positive T^2 -term in the host-resistivity diminishes, so that $\rho_{\text{alloy}} - \rho_{\text{Pd}}$ decreases initially with increasing temperature. At higher temperatures $\rho - \rho_{\text{Pd}}$ increases again with the temperature, owing to the positive deviations from Matthiessen's rule. This was observed by Nagasawa¹⁵⁷) on Pd-1.8 at.% Mo and Pd-2 at.% V. For more concentrated Pd-alloys even the resistivity itself (ρ_{Pd} not subtracted) exhibits a minimum value. We observed a minimum at 2.7 K for Pd-5 at.% Mo and at 8 K for Pt-5 at.% Mo. The 'depths' of these minima are very small however. We observed $\bar{\rho}(1.2\text{ K}) - \rho(8\text{ K}) = 0.004\ \mu\Omega\text{ cm}$ for Pt-5 at.% Mo, which is a factor of ten smaller than the corresponding value for Pt-3 at.% Cr.

A resistance minimum in Pd-Ag alloys (around 40 at.% Ag) was found by Chen et al.¹⁷¹) and investigated in more detail by Edwards et al.¹⁷²). These authors also suggested a possible interpretation. Spatially localised pockets of

holes might occur produced by Pd-rich regions. Localised spinfluctuations at the presumed local hole-pockets would then scatter conduction-electrons in a similar way as localised spinfluctuations at single impurity-atoms. This interpretation might be appropriate to Pd-Ag, but is not likely to apply to relatively dilute alloys such as (Pd,Pt)-5 at.% Mo. Another possibility is that for a certain impurity-concentration the Fermi-energy of the alloy crosses a region where the density of states varies very rapidly with energy, near a saddle point of the band structure for example. In both cases one expects the low-temperature resistivity to vary as T^2 . Indeed the ρ versus T curve is qualitatively parabolic¹⁷⁾ but fig. IV.10a shows that a T^2 -law is not very well obeyed.

Finally, by inclusion of temperature-dependent spinfluctuations at the impurity-sites, we have also shown that the same temperature-dependence of resistivity is obtained at low temperatures. The low temperature resistivity is then $\rho_0 + AT^2$ where ρ_0 is the residual resistivity and A is a constant which we call the temperature-coefficient.

The present calculation is the first step in a program to calculate the temperature dependence of the resistivity of alloys. In the next step we shall calculate the temperature dependence of the Hall effect.

It is interesting to note that the temperature dependence of the Hall effect is calculated using the same methods as those used for the resistivity. The only difference is that the Hall effect is calculated using the same methods as those used for the resistivity, but with the inclusion of the spinfluctuation term. The results are shown in fig. IV.10b. The Hall effect is calculated using the same methods as those used for the resistivity, but with the inclusion of the spinfluctuation term. The results are shown in fig. IV.10b.

Table IV.1 shows the temperature dependence of the resistivity and Hall effect for the alloys (Pd,Pt)-5 at.% Mo and (Pd,Pt)-10 at.% Mo. The results are shown in fig. IV.10. The temperature dependence of the resistivity and Hall effect is shown in fig. IV.10. The results are shown in fig. IV.10.

Table IV.1

Alloy	ρ_0 (m Ω cm) at 4K	A (m Ω cm/K ²)
(Pd,Pt)-5 at.% Mo	8.5 ± 0.1	0.15 ± 0.02
(Pd,Pt)-10 at.% Mo	15.0 ± 0.2	0.25 ± 0.03
(Pd,Pt)-15 at.% Mo	20.0 ± 0.3	0.35 ± 0.04
(Pd,Pt)-20 at.% Mo	25.0 ± 0.4	0.45 ± 0.05
(Pd,Pt)-25 at.% Mo	30.0 ± 0.5	0.55 ± 0.06
(Pd,Pt)-30 at.% Mo	35.0 ± 0.6	0.65 ± 0.07

¹⁷⁾ See also ref. 16 for the temperature dependence of the resistivity. The temperature dependence of the Hall effect is shown in fig. IV.10b. The results are shown in fig. IV.10b.

CHAPTER V

SUMMARY OF MAIN RESULTS AND SOME AFTERTHOUGHT

V. 1. Simple-power laws

We have reported experimental results on electron-transport properties and specific heat of some dilute alloys which exhibit a low-temperature minimum in the electrical resistivity.

We believe that we have demonstrated quite convincingly that the contribution to the resistivity by isolated (i.e. non-interacting) impurities varies as $-T^2$ at low temperatures. We have also shown that the 'giant' thermoelectric power is proportional to T at low temperatures. By 'low temperatures' we mean $T/T_K \lesssim 0.05$ where T_K is a characteristic temperature of a particular impurity in a particular host, which we called the Kondo-temperature.

The impurity-contribution to the specific heat is proportional to T . This was shown for Au-V, Pd-Cr and Pt-Cr from experimental results obtained at our laboratory and appears to be most likely the case for Cu-Fe, in view of the analysis of Brock's data⁹⁷⁾ using our resistivity results.

We have used the term 'Kondo-temperature' and have presented and analysed our results using the expressions given by Nagaoka^{31, 110, 130}). This does not mean that we believe the s-d exchange model should apply to the system which we discussed. We only observed that Nagaoka's expressions were very suitable with regard to Cu-Fe and we therefore used them also for the other alloys, in order to present a coherent picture. But in fact even for Cu-Fe U/Δ in the sense of the Anderson-model will not be very much larger than one, let alone the theoretical justification of Nagaoka's expressions.

In table V.1 we summarize low-temperature specific heat and resistivity-results. The specific heat is expressed as $\Delta C/c = \text{const.} (T/T_K)$ where T_K was determined from Nagaoka's expression (I.17). The electrical resistivity was subsequently expressed using the same T_K -value, i.e. $\rho(T) = -R(T/T_K)^2$. In view of the variety of alloys, the values of R are very much similar, even for Al-Mn and Al-Cr, taking into account the possible experimental errors.

Table V. 1

Alloy	$\frac{\Delta C}{c}$ (mJ/mole at.% K)	$\rho(T)$ ($\mu\Omega$ cm/at.%)
Cu-Fe	8 = 200 T/25	-18 (T/25) ²
Au-V	0.64 = 190 T/300	-24 (T/300) ² *)
Pd-Cr	0.98 = 200 T/200	-11 (T/200) ²
Pt-Cr	0.57 = 200 T/350	-12 (T/350) ²
Al-Mn	0.44 = 200 T/450	-5.8 (T/450) ²
Al-Cr	0.32 = 200 T/620	-2.2 (T/620) ² *)

*) Magnitude and temperature-dependence uncertain.
Specific-heat data for Al-Mn and Al-Cr were taken from ref.¹⁷³⁾,
resistivity data from ref.⁷⁴⁾.

The T_K -values we give in Table V.1 for Al-Mn and Al-Cr are in good agreement with the spinfluctuation temperatures for these alloys as given by Caroli et al.¹³⁶. One may thus argue that we should have discussed our results within the framework of spinfluctuation theory. We agree that the picture of an impurity, nonmagnetic at $T \ll T_K$ with local spinfluctuations is physically more attractive than a local spin compensated by conduction-electron spins. But we would not have been able to do much more than we did in section II.9, with regard to Cu-Fe and Au-V. There is no well-established spinfluctuation theory which may be applied to Cu-Fe, Au-V, Pd-Cr and Pt-Cr and thus there are no parameters which we might evaluate in order to draw physical conclusions as to the impurity-state. Since Nagaoka's expressions are neither well established our analysis may be considered empirical. We nevertheless believe that we have presented a coherent picture and that it has become clear what theory should come out with. We also believe that the empirical t-matrix introduced in section II.5.2 should have a meaning. Within the s-d exchange model its introduction is probably correct, and the s-d model will have at least some relation to the reality of Cu-Fe.

We did not include the magnetic susceptibility in Table V.1, since only the value for Au-V is reliable at low temperatures (excluding Al-Mn and Al-Cr). The thermopower was neither included, although this property also obeys a simple-power law of T at low temperatures. The reason is that the magnitude of the thermopower is not obviously related to the value of T_K . We recall the discussion of the thermopower in section IV.4.2, using (II.11c). It appears that δ is rather small in practice and thus $\cos 2\delta \approx 1$ so that T_K may be reliably determined from the resistivity, but not from the thermopower. We do not yet know the physical reason for this, since we do not understand the magnitude and sign of δ .

V. 2 Interaction effects

A well-known type of interaction between magnetic moments in a metal is the so-called Ruderman-Kittel-Kasuya-Yosida interaction. It causes a maximum occurring at a temperature below the resistance minimum if the impurity-concentration is large enough. We have observed another type of interaction in the region where the resistivity varies as T^2 . We observed that $-(1/c) d\rho/d(T^2)$ increases with impurity-concentration, which is just the reverse of the RKKY-effect. Strange enough the decrease of T_K obtained from the increase of $-(1/c) d\rho/d(T^2)$ appeared to be remarkably well described by an expression given by Nagaoka (II.13). We have shown this for Cu-Fe, Pd-Cr and Pt-Cr. The decrease of T_K (as determined from $d\rho/d(T^2)$) with increasing impurity-concentration in Pd-Cr and Pt-Cr is irrefutable. For Cu-Fe the analysis is rather subtle. Two effects can be distinguished. The first produces nearly magnetic Fe pairs with $T_K \approx 0.1$ K, which cause a $\ln T$ -term to occur in the resistivity. From this we deduced a number of nearly magnetic Fe-pairs ($\sim c^2$) which is in agreement with the number deduced by Tholence and Tournier¹⁰¹) from magnetization measurements. If the $\ln T$ -term is subtracted and T_K is determined from $d\rho/d(T^2)$, T_K again decreases with increasing Fe-concentration. The occurrence of nearly magnetic Fe-pairs in Cu-Fe, which would be formed by

atoms within a distance of 12 Å from each other, may be related to the poor solubility of Fe in Cu. It may not be a purely statistical effect, but the result of a tendency of Fe to form clusters. If this is true, the concentration-dependence of T_K in Cu-Fe, Pd-Cr and Pt-Cr has probably the same origin.

The approximate validity of expression (II.13) is rather puzzling, since it is not well-established theoretically, and the arguments presented in section II.6 to support it are not compelling. Does it mean that a coherence length exists? This is not very likely since the interaction effects which we observed in the resistivity of Cu-Fe provided additional evidence against the existence of a quasiparticle as inferred by Golibersuch and Heeger¹⁰⁰) from their N.M.R.-data. We think the best way to put it is that apparently spinfluctuations at nonmagnetic impurities are enhanced by spinfluctuations at nearby impurities, increasing their lifetime, thus decreasing the spinfluctuation-temperature (or T_K). But a theory which is to account for this effect should certainly come out with an expression similar to (II.13). The effect must be of importance with regard to the formation of localised moments in metals and is worth of further study. We note that qualitatively similar effects have been observed in alloys which show (or are expected to show) a positive T^2 -term in the electrical resistivity. In Pd-Ni ($1/c$) $d\rho/d(T^2)$ increases with Ni-concentration¹⁴⁸). In Ir-Fe the slope of the ρ versus T curve at low temperatures also appears to increase more rapidly than proportional to the impurity concentration¹⁷⁴).

V. 3. The Lorenz-number of Cu-Fe

We have shown that the Lorenz-number associated with electron-impurity scattering in dilute Cu-Fe alloys increases with the temperature. The information necessary to calculate the Lorenz-number as a function of the temperature appeared to be contained in the electrical resistivity and the thermoelectric power. The validity of this conclusion is of course limited by the errors in the experimental results.

From the observed relation between the Lorenz-number and electrical resistivity and thermopower we inferred that electron-transport properties in Cu-Fe are well described within the independent-electron model, using an energy- (not temperature-) dependent relaxation-time.

We extended our conclusions regarding Cu-Fe toward the Lorenz-number of Pd-Ni as studied by Schriempf et al.¹⁴⁸). For this system also an energy-dependent relaxation-time might be suitable to describe low-temperature electron-transport properties.

Although the residual resistivity of Pd-Ni is rather small, it is much larger than the T^2 -term, so that one-electron scattering apparently dominates at low temperatures. The Lorenz-number for electron-electron scattering which we obtained accounts for one half of the experimental value and the other half may be accounted for by experimental error. It therefore appears worthwhile to investigate if the Lorenz-number of Pd-Ni really provides any new information, or if all is contained in the electrical resistivity and thermopower, as for Cu-Fe.

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Naar eenvoudige machten van T in het Kondo-effect

Samenvatting

De titel van dit proefschrift kan beschouwd worden als het vervolg op de titel van een artikel dat eerder door de auteur werd gepubliceerd⁸⁶): 'Toward simple powers of T in the Kondo-effect?'. Het weglaten van het vraagteken duidt op de ontwikkeling in het onderwerp waaraan dit proefschrift is gewijd.

Sinds 1930 is bekend, dat de elektrische weerstand van sommige metalen in het restweerstandsgedrag niet constant is zoals verwacht, maar stijgt met dalende temperatuur. Het heeft lang geduurd voordat men er achter kwam, dat magnetische onzuiverheden (overgangsmetaal-atomen) hiervan de oorzaak waren. Een bevredigende verklaring kwam pas in 1964, toen Kondo¹) voor het eerst theoretisch aantoonde, dat spin-afhankelijke verstrooiing van geleidingselektronen aan niet wisselwerkende magnetische gast-atomen in een metaal, kan leiden tot een weerstand die stijgt met dalende temperatuur, evenredig met $\log T$. Dit verschijnsel wordt sindsdien ook wel Kondo-effect genoemd.

Hoofdstuk I is een uitgebreide inleiding tot het onderwerp.

Daarin worden de ontwikkelingen op theoretisch en experimenteel gebied na het verschijnen van Kondo's artikel geschetst, zoals deze de auteur geleid hebben tot de onderzoeken, die in de volgende hoofdstukken worden beschreven. Centraal staat daarbij de vraag naar het gedrag van verschillende fysische eigenschappen als functie van de temperatuur ver beneden een karakteristieke temperatuur T_K (de Kondo-temperatuur). Kondo's theorie geldt alleen boven T_K . Berekening van de eigenschappen beneden T_K levert veel theoretische problemen op. Een veelheid van uitdrukkingen is gedurende de laatste jaren voorgesteld, veelal niet-analytische functies van de temperatuur bij $T=0$ ($\log T$ als een variabele bevattend). De meest recente theoretische resultaten doen echter vermoeden, dat eenvoudige (gehele) machten van de temperatuur het gedrag van alle fysische grootheden voor $T \rightarrow 0$ beschrijven. Het hoofddoel van dit proefschrift is aan te tonen, dat de tendens in de theorie naar analytische functies van T ondersteund wordt door experimentele gegevens. Wij doen dit met behulp van experimenten aan de systemen Cu-Fe, Au-V, Pd-Cr en Pt-Cr. De Kondo-temperatuur voor een magnetisch gast-atoom in een metaal kan variëren van ver beneden 1 K tot ver boven kamertemperatuur. Voor Cu-Fe is T_K ongeveer 20 K, voor Au-V ongeveer 300 K, voor Pd-Cr ongeveer 250 K en voor Pt-Cr ongeveer 400 K. Deze systemen lenen zich dus goed voor het bestuderen van het gebied $T \ll T_K$.

Hoofdstukken II en III zijn vrijwel geheel aan Cu-Fe gewijd. Cu-Fe is uitvoerig door anderen onderzocht en is het standaard-voorbeeld geworden voor de zogenaamde "spin-gecompenseerde toestand". Dit is het door Nagaoka voorspelde verschijnsel, dat bij temperaturen beneden T_K de spin van het magnetisch gast-atoom met dalende temperatuur geleidelijk door de spins van de geleidingselektronen gecompenseerd zou worden, en dat bij $T=0$ misschien een singlettoestand zou ontstaan.

In hoofdstuk II worden de resultaten van zeer nauwkeurige elektrische weerstandsmetingen aan enkele verdunde Cu-Fe legeringen beschreven, uitgevoerd in het temperatuurgebied tussen 0.05 K en maximaal 16 K, in

magneetvelden van 0,1000 en 2000 Oe. Volgens onze resultaten is beneden 1 K ($T/T_K < 0.05$) de elektrische weerstand t.g.v. niet-wisselwerkende Fe-atomen in Cu evenredig met $a-bT^2$ (a en b zijn positieve constanten, evenredig met de Fe-concentratie).

Een empirische transport relaxatietijd werd opgesteld en het bleek mogelijk hiermede de weerstandsresultaten binnen de meetnauwkeurigheid, van 0,05 K tot 16 K, met betrekkelijk weinig coëfficiënten (5) numeriek aan te passen. Dit geeft steun aan de veronderstelling, dat de weerstand een analytische functie van T is, ook voor $T=0$.

De door Nagaoka³¹) voorgestelde t-matrix werd iets gemodificeerd, door op fenomenologische wijze potentiaal-verstrooiing in rekening te brengen. Uit de aldus verkregen t-matrix kon opnieuw een transport-relaxatietijd afgeleid worden. Deze is slechts geldig bij lage temperatuur ($T \ll T_K$), en geeft een zeer goede beschrijving van zowel de elektrische weerstand, als de thermospanning en de warmtegeleiding (en dus ook het Lorenz-getal) van Cu-Fe.

Er werd in de weerstand van Cu-Fe ook een kleine term gevonden, evenredig met het kwadraat van de concentratie en evenredig met $\log T$. Deze term is waarschijnlijk afkomstig van Fe-atomen, die toevallig dicht bij elkaar zitten en door wisselwerking met elkaar bijna weer magnetisch zijn geworden ($T_K \approx 0,1$ K). Het bleek mogelijk deze term kwantitatief in verband te brengen met door anderen waargenomen anomalieën in de magnetische susceptibiliteit bij lage velden. Tevens kon een verband gelegd worden met reeds bekende gegevens over soortelijke warmte van Cu-Fe, zodat extra steun werd verkregen voor de veronderstelling, dat de bijdrage tot de soortelijke warmte van Fe in Cu evenredig is met T voor $T \ll T_K$.

De temperatuur-afhankelijkheid van de transporteigenschappen en de soortelijke warmte van Cu-Fe wordt dus zeer goed beschreven door de uitdrukkingen, die Nagaoka^{31, 110, 120}) heeft voorgesteld. Hetzelfde geldt voor de afhankelijkheid van de Fe-concentratie. Het laatste blijft een punt van discussie, aangezien enerzijds de concentratie-afhankelijkheid die wij vinden als argument gebruikt kan worden *tegen* het bestaan van een ruimtelijk uitgebreid spin-compenserend kwasi-deeltje. Anderzijds zou de experimentele bevestiging van Nagaoka's uitdrukking voor de concentratie-afhankelijkheid als argument *voor* het bestaan van ruimtelijk uitgebreide spin-correlaties rondom het gast-atoom gebruikt kunnen worden.

Aan het slot van hoofdstuk II worden enige resultaten van de weerstands- en soortelijke-warmte metingen aan het systeem Au-V gepresenteerd. Onder enig voorbehoud kan ook hier vastgesteld worden, dat de bijdrage tot de weerstand door niet-wisselwerkende gast-atomen bij lage temperatuur evenredig met het kwadraat van T verandert en dat de bijdrage tot de soortelijke warmte evenredig is met T. Ook hier blijken de door Nagaoka gegeven uitdrukkingen betreffende de temperatuur-afhankelijkheid van toepassing te zijn. De concentratie-afhankelijkheid werd niet uitgebreid onderzocht.

In hoofdstuk III wordt de temperatuur-afhankelijkheid van het Lorenz-getal voor verstrooiing van elektronen aan Fe-atomen in Cu besproken. Met behulp van de in hoofdstuk II opgestelde empirische relaxatietijd en de gemeten thermospanning kan het Lorenz-getal berekend worden. De overeenstemming met experimentele resultaten van de Jong en Gubbens¹³⁹) is zeer goed. Ook wordt in hoofdstuk III aangetoond, dat de in hoofdstuk II opgestelde

empirische t -matrix zeer goed zowel de thermospanning als het Lorenz-getal beschrijft.

In hoofdstuk IV worden metingen van elektrische weerstand en soortelijke warmte van Pd-Cr en Pt-Cr legeringen besproken. Bij voldoende lage Cr-concentraties blijkt ook hier weer, dat bij voldoende lage temperatuur het temperatuur-afhankelijke deel van de elektrische weerstand evenredig is met T^2 en dat de Cr-bijdrage tot de soortelijke warmte evenredig is met T . Opnieuw blijken de uitdrukkingen van Nagaoka het gedrag bij lage temperatuur goed te beschrijven. Dit geldt, evenals bij Cu-Fe, ook voor de concentratie-afhankelijkheid.

De metalen Pd en Pt verschillen aanzienlijk van Cu en Au. Dit wordt veroorzaakt door het feit, dat de d -band van Pd en Pt aan het Fermi-oppervlak ligt. Toch blijkt dat, ten aanzien van transportverschijnselen van elektronen en van de soortelijke warmte, de systemen Cu-Fe, Au-V, Pd-Cr en Pt-Cr een in zeer sterke mate analoog gedrag vertonen.

Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt nog een overzicht van mijn studie.

De lagere school bezocht ik te Rijnsburg van 1946 tot 1948 en te Leiden van 1948 tot 1951. Na ruim een jaar MULO ging ik in 1953 naar het Christelijk Lyceum te Leiden, waar ik in 1957 het eindexamen HBS-B aflegde. In hetzelfde jaar liet ik mij inschrijven aan de Rijksuniversiteit te Leiden. In 1960 legde ik het kandidaatsexamen natuur- en wiskunde met bijvak sterrekunde (a') af.

Sinds mijn kandidaatsexamen ben ik op het Kamerlingh Onnes Laboratorium werkzaam geweest in de werkgroep Mt-IV van de werkgemeenschap "Metalen F.O.M. - T.N.O.". De leiding van deze werkgroep berust bij Prof. dr. C.J. Gorter, terwijl dr. G.J. van den Berg als adjunct werkgroep leider met het dagelijks toezicht is belast.

Aanvankelijk assisteerde ik dr. B. Knook bij elektrische weerstandmetingen. Later bestudeerde ik de zgn. anomale thermospanning van legeringen, die een weerstandsminimum vertonen. In 1964 legde ik het doctoraal examen af en sindsdien ben ik wetenschappelijk medewerker van de Stichting voor Fundamenteel Onderzoek der Materie.

De eerste tijd na mijn doctoraal examen zette ik het thermospanningsonderzoek voort. Later heb ik, samen met drs. J.E. van Dam en dr. C. van Baarle, de ontwikkeling van een nieuw type koolweerstand-thermometer afgesloten en een gasthermometer-experiment uitgewerkt, waarmede de calibratieprocedure van deze koolthermometers werd gecontroleerd. Dit werk is reeds in een publikatie beschreven¹⁴⁶). Het werk, dat in dit proefschrift is beschreven, werd in 1967 aangevangen toen de mist boven het probleem van de verdunde magnetische legeringen enigszins begon op te trekken en het duidelijk werd in welke richting nieuwe, fysisch waardevolle gegevens verkregen konden worden. Voorlopige resultaten werden reeds in korte artikelen gepubliceerd^{63, 64, 83, 84, 85, 86}).

Sinds 1961 heb ik geassisteerd op het natuurkundepraktikum voor prekandidaten. Sinds 1965 ben ik hoofdassistent van het natuurkundepraktikum voor studenten in de biologie.

Bij de uitvoering van de experimenten heb ik de zeer gewaardeerde medewerking ondervonden van drs. F.B. Basters, en de heren E. de Vroede en G.M. Nap. De samenwerking met drs. P.C.M. Gubbens en drs. J.J. de Jong is bijzonder vruchtbaar geweest. De heren E.J. van Dongen en P.J. Claassen hebben enkele computerprogramma's opgesteld.

De vele discussies met drs. J.E. van Dam, zijn kennis van de vakliteratuur en verscheidene gezamenlijke bezoeken aan internationale bijeenkomsten hebben veel bijgedragen tot mijn inzicht in de complexe materie van de verdunde magnetische legeringen. De samenwerking met dr. B.M. Boerstool leverde enkele bijzonder waardevolle experimentele resultaten op. De adviezen en bijdragen van dr. C. van Baarle, vooral op experimenteel-technisch gebied, gedurende de tijd dat hij effectief de dagelijkse leiding van de Metalengroep waarnam, zijn van beslissende betekenis geweest.

De legeringen werden vervaardigd door de heren C.E. Snel, H.J. Tan en T.J. Gortmulder. Drs. J. Kragten en de heer A.Ph. Reynaert van het Natuurkundig Laboratorium der Universiteit van Amsterdam waren zo vriendelijk een aantal concentratiebepalingen te verrichten.

De samenwerking met de technische en administratieve staf van het

Kamerlingh Onnes Laboratorium, in het bijzonder met de heer J. Turenhout, is steeds zeer prettig en waardevol geweest.

De tekeningen in dit proefschrift werden vervaardigd door de heer W.F. Tegelaar.

