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ON THE ORIGIN OF THE GIANT THERMOPOWERS IN SOME METALS AT LOW TEMPERATURES

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Synopsis

A mechanism is proposed which yields large values of the thermopower approaching $\kappa/e = 86\ \mu V$/degree under favourable circumstances. These appear in metals for which the well-known anomalies in the electronic properties caused by transition metal impurities have been observed. The distribution function in the presence of an electric field has a current carrying part which is strongly asymmetric with respect to the Fermi level. This leads to a first order Peltier heat current and hence, by Kelvin's relation, to a first order thermopower. The possibilities of the mechanism are demonstrated for the Yosida model. Any model in which there is a polarisation in some way of the transition metal ions over distances of the order of the electronic mean free path will yield high values of the thermopower. The electrical resistivity in the Yosida model is only slightly modified by the strong energy dependence of the effective relaxation time.

1. *Introduction*. Copper, silver, gold and a few other metals tend to display anomalies in their electron properties at low temperatures. Addition to "pure" copper of small amounts of diamagnetic impurities gives an initial increase of the anomalies, e.g. the negative temperature coefficient of the resistivity and the enormous values of the thermopower [1]). It is not difficult to devise models of magnetically interacting *transition metals* dissolved in copper etc. which are capable of producing anomalies in the transport properties. A few years ago one of the authors [2]) suggested that all these anomalies in alloys of copper with small amounts of lead, germanium, tin, nickel and other diamagnetic impurities were caused in some way by traces of iron or other impurities with unfilled d-shells [2]). Recently Gold *e.a.* [3]) put forward the idea that tin liberates iron from its oxide usually present even in the purest copper available. They arrived at a good deal of consistency in the observed thermopower and negative temperature coefficients in the diluted alloys.

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*) The computational part of this paper [illegible] Report R 543.

Yosida [4]), expanding the former ideas of Schmitt [5]), calculated the resistivity due to transition metal ions. The interaction between the latter was described by a sort of Weiss field, acting on the ions. He arrived at a temperature dependent residual resistivity which had, however, a positive temperature coefficient. Dekker [6]) and Brailsford and Overhauser [7]) started with exchange coupled ion pairs and found a resistivity which initially increased with decreasing temperature to reach a saturation value near absolute zero in a monotonic way or after having passed through a maximum. The anomalous part should be in proportion to the square the concentration, which seems to be in disagreement with the experimental results unless one takes "isolated" ions of the Yosida model into account [7]). Overhauser [8]) put forward the idea of spin density waves stabilized by the presence of magnetic impurities. His main result, that the ion spin specific heat is proportional to the temperature and independent of the concentrations, can (Marshall [9])) also be described by a distribution of Yosida's internal fields. It should be noted that at concentrations below 1 per cent a single internal field accounts for the specific heat rather well [10]).

Theories for the anomalous behaviour of magnetic ions in the noble metals are usually compared with the electrical resistivity and specific heat. The magnitude of the thermopower in these alloys deserves some attention since it is larger than the Sommerfeld theory can explain by many orders of magnitude.

The purpose of this paper is to discuss the question of how certain features of the scattering by magnetic impurities, which have been neglected so far, lead to enormous values of the thermopower. This will be demonstrated with a revised Yosida model. Although this research was started with the anomalies in thermopower in mind, it was hoped that a minimum and/or a maximum could be found in the electrical resistivity. Similar modifications of the Boltzmann equation should also be applied to the theories of Dekker [6]) and of Brailsford and Overhauser [7]) but, in contrast to Yosida's model or an extension thereof, their model is impotent to give giant values of the thermopower.

2. *Derivation of a modified Boltzmann equation for the Yosida model.* The scattering potential of electrons in a metal caused by a magnetic impurity at $\boldsymbol{r} = 0$ is

$$H = V(\boldsymbol{r}) - 2J(\boldsymbol{r})(\boldsymbol{s}\,.\,\boldsymbol{S}), \tag{1}$$

where $\boldsymbol{s}$ and $\boldsymbol{S}$ are the spin operators of electron and magnetic ion respectively. We follow Yosida [4]) except for the influence of the Pauli exclusion-principle.

In eq. (1) the first term represents the conventional scattering, the second one the exchange part of it. It is assumed that the ion feels an effective field H

in the ζ direction. The energy levels of the ion are given by $mg\mu_B H = m\Delta$, where the magnetic quantum number m ranges from $-S$ to $+S$. The population of the level m is proportional to $\exp -m\Delta/\kappa T$, and hence the probability w_m that the ion is in the state m equals

$$w_m = e^{-m\mu} / \sum_{m=-S}^{S} e^{-m\mu}; \quad \mu = \Delta/\kappa T. \tag{2}$$

With the abbreviations $s^{\pm} = s_\xi \pm i s_\eta$ and $S^{\pm} = S_\xi \pm i S_\eta$, where s_ξ, s_η, s_ζ and S_ξ, S_η, S_ζ are the spin operators for electron and ion, eq. (1) can be written as:

$$H = V(\boldsymbol{r}) - J(\boldsymbol{r})(2 s_\zeta S_\zeta + s^+ S^- + s^- S^+). \tag{3}$$

The second term describes transitions without spin flips which are therefore elastic but depend on the spin state of electron and ion. The only non-zero matrix elements of s_ζ and S_ζ are $(s_\zeta)_{\pm\pm} = \pm\frac{1}{2}$ and $(S_\zeta)_{mm} = m$. The matrix elements of the second and of the first term in eq. (3) must be combined in order to get the quantum mechanical transition probabilities for the elastic transitions

$$W(\boldsymbol{k}\pm, m; \boldsymbol{k}'\pm, m) = |V_{\boldsymbol{k}'\boldsymbol{k}} \mp m J_{\boldsymbol{k}'\boldsymbol{k}}|^2 \, D(E_{\boldsymbol{k}'} - E_{\boldsymbol{k}}), \tag{4}$$

which are different for electrons with $+$ and $-$ spin. The function D takes care of energy-conservation. The transition probabilities from the terms in eq. (3) have some coefficients in common and these are contained in the function D.

The third and fourth term in eq. (3) cause spin flips of electron and ion which are inelastic in the electron energy. A spin operator with $+$ $(-)$ as index increases the magnetic quantum number by $+1$ (-1). Hence the sum of the magnetic quantum numbers of electron and ion is conserved. The only non-zero matrix elements have as squared absolute values

$$|S^{\pm}_{m\pm 1, m}|^2 = S(S+1) - m(m \pm 1), \tag{5}$$

which result is also valid for electrons ($S = \frac{1}{2}$, $m = \pm\frac{1}{2}$).

The quantum mechanical transition probability by the third term in eq. (3) is

$$W(\boldsymbol{k}-, m; \boldsymbol{k}'+, m-1) = |J_{\boldsymbol{k}'\boldsymbol{k}}|^2 \{S(S+1) - m(m-1)\} \, D(E_{\boldsymbol{k}'} - E_{\boldsymbol{k}} - \Delta). \tag{6}$$

For these transitions the electron energy increases with Δ since the ion energy decreases with Δ. The fourth term causes transitions for which the electron spin changes from $+$ to $-$ and the electron energy decreases with Δ.

$$W(\boldsymbol{k}+, m; \boldsymbol{k}'-, m+1) = |J_{\boldsymbol{k}'\boldsymbol{k}}|^2 \{S(S+1) - m(m+1)\} \, D(E_{\boldsymbol{k}'} - E_{\boldsymbol{k}} + \Delta). \tag{7}$$

For the total transition probability P one has to average over m with w_m as weight and to take the Pauli exclusion principle into account.

This gives

$$P(\boldsymbol{k}+\to\boldsymbol{k}'+)=\sum_m |V_{\boldsymbol{k}'\boldsymbol{k}}-mJ_{\boldsymbol{k}'\boldsymbol{k}}|^2 w_m f_{\boldsymbol{k}}^+ (1-f_{\boldsymbol{k}'}^+)\, D(E_{\boldsymbol{k}'}-E_{\boldsymbol{k}}), \tag{8a}$$

$$P(\boldsymbol{k}-\to\boldsymbol{k}'-)=\sum_m |V_{\boldsymbol{k}'\boldsymbol{k}}+mJ_{\boldsymbol{k}'\boldsymbol{k}}|^2 w_m f_{\boldsymbol{k}}^- (1-f_{\boldsymbol{k}'}^-)\, D(E_{\boldsymbol{k}'}-E_{\boldsymbol{k}}), \tag{8b}$$

$$P(\boldsymbol{k}-\to\boldsymbol{k}'+)=\sum_m |J_{\boldsymbol{k}'\boldsymbol{k}}|^2\{S(S+1)-\\ -m(m+1)\}\, w_{m+1} f_{\boldsymbol{k}}^- (1-f_{\boldsymbol{k}'}^+)\, D(E_{\boldsymbol{k}'}-E_{\boldsymbol{k}}-\Delta), \tag{8c}$$

$$P(\boldsymbol{k}+\to\boldsymbol{k}'-)=\sum_m |J_{\boldsymbol{k}'\boldsymbol{k}}|^2\{S(S+1)-\\ -m(m+1)\}\, w_m\ f_{\boldsymbol{k}}^+ (1-f_{\boldsymbol{k}'}^-)\, D(E_{\boldsymbol{k}'}-E_{\boldsymbol{k}}+\Delta), \tag{8d}$$

where $f_{\boldsymbol{k}}^+$ is the probability that the electron state $\boldsymbol{k}$ with $+$ spin is occupied, etc. In eq. (8*c*) $m+1$ was substituted for m in order to make the spin matrix element the same as in eq. (8*d*).

Using eq. (8) the scattering terms in the Boltzmann equations for the $+$ and $-$ spin electrons with wavenumber $\boldsymbol{k}$ are

$$\left(\frac{\partial f_{\boldsymbol{k}}^+}{\partial t}\right)_{\text{scatt}} = \sum_{\boldsymbol{k}'}\{P(\boldsymbol{k}'+\to\boldsymbol{k}+)-P(\boldsymbol{k}+\to\boldsymbol{k}'+)\}+\\ +\{P(\boldsymbol{k}'-\to\boldsymbol{k}+)-P(\boldsymbol{k}+\to\boldsymbol{k}'-)\}, \tag{9a}$$

$$\left(\frac{\partial f_{\boldsymbol{k}}^-}{\partial t}\right)_{\text{scatt}} = \sum_{\boldsymbol{k}'}\{P(\boldsymbol{k}'-\to\boldsymbol{k}-)-P(\boldsymbol{k}-\to\boldsymbol{k}'-)\}+\\ +\{P(\boldsymbol{k}'+\to\boldsymbol{k}-)-P(\boldsymbol{k}-\to\boldsymbol{k}'+)\}. \tag{9b}$$

For a spherical Fermi surface with $E_{\boldsymbol{k}}=\hbar^2|\boldsymbol{k}|^2/2m$, the influence of an electric field F in the x-direction on the distribution function gives the drift term

$$\left(\frac{\partial f_{\boldsymbol{k}}}{\partial t}\right)_{\text{drift}} = \frac{\hbar e F}{m}\frac{\partial f_\eta^0}{\partial \eta}\frac{k_x}{\kappa T}, \tag{10}$$

with

$$f_\eta^0=(e^\eta+1)^{-1} \quad\text{and}\quad \eta=(E_{\boldsymbol{k}}-\zeta)/\kappa T. \tag{11}$$

Eq. (10) suggests the "Ansatz", as usual,

$$f_{\boldsymbol{k}}^\pm = f_\eta^0 + \frac{k_x}{\kappa T}\frac{\partial f_\eta^0}{\partial \eta}c_\eta^\pm. \tag{12}$$

Except for the coefficient $\hbar eF/m$, the functions $c_\eta^\pm$ play the part of a relaxation time. Because of the special form of the scattering terms, eq. (9), one expects a strong dependence of c_η on electron energy η. By the substitution of eq. (12) and eq. (8) in eq. (9) one finds after some algebraic manipulations:

$$\left(\frac{\partial f_{\boldsymbol{k}}^+}{\partial t}\right)_{\text{sc}} = (\kappa T)^{-1}\sum_{\boldsymbol{k}'}\overline{|V_{\boldsymbol{k}'\boldsymbol{k}}-mJ_{\boldsymbol{k}'\boldsymbol{k}}|^2}\,(k_x-k_x')\,c_\eta^+ D(E_{\boldsymbol{k}'}-E_{\boldsymbol{k}})\,R(\eta,0)+\\ +(\kappa T)^{-1}\sum_{\boldsymbol{k}'}\overline{\{S(S+1)-m(m+1)\}}\,|J_{\boldsymbol{k}'\boldsymbol{k}}|^2\,(k_x c_\eta^+ - k_x' c_{\eta-\mu}^-)\,\cdot\\ \cdot D(E_{\boldsymbol{k}'}-E_{\boldsymbol{k}}+\Delta)\,R(\eta,-\mu), \tag{13a}$$

$$\left(\frac{\partial f_{\boldsymbol{k}}^-}{\partial t}\right)_{\mathrm{sc}} = (\kappa T)^{-1} \sum_{\boldsymbol{k}'} \overline{|V_{\boldsymbol{k}'\boldsymbol{k}} + mJ_{\boldsymbol{k}'\boldsymbol{k}}|^2}\, (k_x - k_x')\, c_\eta^-\, D(E_{\boldsymbol{k}'} - E_{\boldsymbol{k}})\, R(\eta, 0) +$$
$$+ (\kappa T)^{-1} \sum_{\boldsymbol{k}'} \overline{\{S(S+1) - m(m+1)\}}\, |J_{\boldsymbol{k}'\boldsymbol{k}}|^2\, (k_x c_\eta^- - k_x' c_{\eta+\mu}^+) \cdot$$
$$\cdot D(E_{\boldsymbol{k}'} - E_{\boldsymbol{k}} - \Delta)\, R(-\eta, -\mu). \qquad (13b)$$

The equilibrium distribution terms f_η^0, $\partial f_\eta^0/\partial\eta$ etc. have been incorporated in the function

$$R(\eta, \mu) = (e^\eta + 1)^{-1}\, (e^{-\eta-\mu} + 1)^{-1}$$

and the energy conservation expressed by the D-functions has been used. It has been assumed that the "width of the D-functions" can be taken to be smaller than the width of the electron distribution function $\partial f_\eta^0/\partial\eta$. This may be questionable for inelastic transitions, especially for the calculation of the thermopower. The bars denote averages over m with w_m as weight. By replacing $\sum_{\boldsymbol{k}'}$ by an integration over $\boldsymbol{k}'$,

$$\sum_{\boldsymbol{k}'} \to \int\!\!\int\!\!\int k'^2\, \mathrm{d}k'/\mathrm{d}E_{\boldsymbol{k}'} \sin\delta\, \mathrm{d}\delta\, \mathrm{d}\varphi\, \mathrm{d}E, \qquad (14)$$

and assuming that the matrix elements of V and J depend on the angle δ between $\boldsymbol{k}$ and $\boldsymbol{k}'$ only, eq. (13) becomes

$$\left(\frac{\partial f_{\boldsymbol{k}}^+}{\partial t}\right)_{\mathrm{sc}} = (\kappa T)^{-1}\, k_x \{\int_0^\pi \overline{|V_{\boldsymbol{k}'\boldsymbol{k}} - mJ_{\boldsymbol{k}'\boldsymbol{k}}|^2}\, c_\eta^+ (1 - \cos\delta) \sin\delta\, \mathrm{d}\delta\}\, R(\eta, 0) +$$
$$+ (\kappa T)^{-1}\, k_x \{\overline{S(S+1) - m(m+1)} \int_0^\pi \cdot$$
$$\cdot\, |J_{\boldsymbol{k}'\boldsymbol{k}}|^2\, (c_\eta^+ - c_{\eta-\mu}^- \cos\delta) \sin\delta\, \mathrm{d}\delta\}\, R(\eta, -\mu), \qquad (15a)$$

$$\left(\frac{\partial f_{\boldsymbol{k}}^-}{\partial t}\right)_{\mathrm{sc}} = (\kappa T)^{-1}\, k_x \{\int_0^\pi \overline{|V_{\boldsymbol{k}'\boldsymbol{k}} + mJ_{\boldsymbol{k}'\boldsymbol{k}}|^2}\, c_\eta^- (1 - \cos\delta) \sin\delta\, \mathrm{d}\delta\}\, R(\eta, 0) +$$
$$+ (\kappa T)^{-1}\, k_x \{\overline{S(S+1) - m(m+1)} \int_0^\pi \cdot$$
$$\cdot\, |J_{\boldsymbol{k}'\boldsymbol{k}}|^2\, (c_\eta^- - c_{\eta+\mu}^+ \cos\delta) \sin\delta\, \mathrm{d}\delta\}\, R(-\eta, -\mu). \qquad (15b)$$

The factors common to all the terms in eqs. (15a) and (15b), such as $k^2\, \mathrm{d}k/\mathrm{d}E$ have been neglected again. By the substitution of eqs. (10) and (15) the Boltzmann equation

$$\left(\frac{\partial f_{\boldsymbol{k}}}{\partial t}\right)_{\mathrm{sc}} + \left(\frac{\partial f_{\boldsymbol{k}}}{\partial t}\right)_{\mathrm{drift}} = 0, \qquad (16)$$

yields the system of difference equations, if we neglect common, irrelevant factors

$$1 = \{A + (D - E)\,\overline{m^2} - 2C\overline{m}\}\, c_\eta^+ + P(Dc_\eta^+ - Ec_{\eta-\mu}^-)\, Q(-\eta, \mu), \quad (16a)$$

$$1 = \{A + (D - E)\,\overline{m^2} + 2C\overline{m}\}\, c_\eta^- + P(Dc_\eta^- - Ec_{\eta+\mu}^+)\, Q(\eta, \mu), \quad (16b)$$

where $Q(\eta, \mu) = (e^\eta + 1)(e^{\eta+\mu} + 1)^{-1}$; $P(\mu) = \overline{S(S+1) - m(m+1)}$ (17)

$$A = \int_0^\pi |V(k \sin \delta/2)|^2 \sin \delta (1 - \cos \delta)\, \mathrm{d}\delta$$

$$D = \int_0^\pi |J(k \sin \delta/2)|^2 \sin \delta\, \mathrm{d}\delta$$

$$E = \int_0^\pi |J(k \sin \delta/2)|^2 \sin \delta \cos \delta\, \mathrm{d}\delta$$

$$C = \int_0^\pi Re[V(k \sin \delta/2)\, J^*(k \sin \delta/2)] \sin \delta (1 - \cos \delta)\, \mathrm{d}\delta. \quad (18)$$

From the solution $c_\eta^\pm$ of the Boltzmann equation, eq. (16), follow the electric ($e > 0$) and the reversible heat current

$$I = -e \int_{-\infty}^{+\infty} (c_\eta^+ + c_\eta^-)\, \frac{\partial f_\eta^0}{\partial \eta}\, \mathrm{d}\eta, \quad (19a)$$

$$W = \kappa T \int_{-\infty}^{+\infty} \eta (c_\eta^+ + c_\eta^-)\, \frac{\partial f_\eta^0}{\partial \eta}\, \mathrm{d}\eta, \quad (19b)$$

where the electric current is calculated with eqs. (12) and (14) from $\Sigma_{\boldsymbol{k}} v_{\boldsymbol{k}}(-e)\,(f_{\boldsymbol{k}}^+ + f_{\boldsymbol{k}}^-)$, and the heat current from $\Sigma_{\boldsymbol{k}} v_{\boldsymbol{k}}(E_{\boldsymbol{k}} - \zeta)\,(f_{\boldsymbol{k}}^+ + f_{\boldsymbol{k}}^-)$. Coefficients with a weak η dependence, common to both expressions have been neglected.

Contrary to what is usually done the absolute thermopower S is calculated from the absolute Peltier heat Π. The latter is given by the ratio of the heat current W in eq. (19b) to the electric current I in eq. (19a). Hence, using Kelvin's relation,

$$S = \Pi/T = T^{-1}\, W/I = -(\kappa/e)\, \frac{\int_{-\infty}^{+\infty} \eta (c_\eta^+ + c_\eta^-)\, \frac{\partial f_\eta^0}{\mathrm{d}\eta}\, \mathrm{d}\eta}{\int_{-\infty}^{+\infty} (c_\eta^+ + c_\eta^-)\, \frac{\partial f_\eta^0}{\partial \eta}\, \mathrm{d}\eta}. \quad (20)$$

It can be seen from eq. (20) that the thermopower does not depend on the constant factors which have been neglected systematically in the Boltzmann equations and in eqs. (18) and (19). This constant is needed for the electrical resistivity, but the missing factor can be obtained simply from the well-known result if $J(\boldsymbol{r}) = 0$; moreover the fluctuations of the resistivity as a function of temperature are more interesting than the resistivity itself.

Turning to the Boltzmann equation, eq. (16), which can be written in the form

$$P^+c_\eta^+ + P(Dc_\eta^+ - Ec_{\eta-\mu}^-)\, Q(-\eta, \mu) - \varphi_1(\eta, \mu) = 1 \tag{22a}$$

$$P^-c_\eta^- + P(Dc_\eta^- - Ec_{\eta+\mu}^+)\, Q(\eta, \mu) - \varphi_2(\eta, \mu) = 1, \tag{22b}$$

where $\quad P^\pm = A + (D - E)\, \overline{m^2} \mp 2C\overline{m} \quad$ and $\quad P^+(\mu) = P^-(-\mu)$,

the elastic scattering terms and the inelastic terms with spin flip-flops are easily recognized as the terms with $P^\pm$ and P respectively. Taking $P^+ = P^- = 0$, it follows from eq. (22) that c_η^+ depends on η; $c_\eta^+ = c_{-\eta}^-$, however, hence the integral W vanishes and the thermopower S becomes zero. For a finite S the elastic terms are also needed. These are different for + and − spin electrons. The two types of terms combined make $c_\eta^+ + c_\eta^-$ asymmetric with respect to $\eta = 0$. The maximum asymmetry in $c_\eta^+ + c_\eta^-$ will occur for $\mu \approx 1$ or $T \approx \Delta/\kappa$. For $C = \sqrt{A(D-E)}$ and $(D - E) = 0.1\ A$ it is expected that at $T \approx \Delta/\kappa$

$$(c_1^+ + c_1^-) - (c_{-1}^+ + c_{-1}^-) \approx 0.1\ (c_0^+ + c_0^-).$$

In this case eq. (20) gives a thermopower with an absolute value approaching $\kappa/e = 86.3\ \mu V/\text{degree}$ under favourable conditions. This result should be compared to that for *normal* scattering where the energy dependence of the "scattering time" may be expressed by

$$c_\eta = c_0(1 + p\eta\kappa T/\zeta) \quad \text{with} \quad |p| \approx 1. \tag{21}$$

This leads to $S = p'(\kappa/e)(\kappa T/\zeta)$, with $|p'| \approx |p|$, which is therefore negligible ($\zeta/\kappa \approx 10^5$) compared to the value which is expected from eq. (20) in the case that $c_\eta^\pm$ are strong functions of η.

The solutions of eq. (16) depend on $\mu = \Delta/\kappa T$, hence the resistivity will in general depend on temperature. Yosida's equations can be obtained from eq. (16) by the substitution of $Q(0, \mu)$ for $Q(\eta, \mu)$ and the neglect of the η-dependence of $c_\eta^\pm$.

For the sake of simplicity one single ion has been assumed to be present. Now it is a simple matter to extend the equations to the case where a fraction n of the ions experiences a field $+\mu$ and the other fraction, $1 - n$, a field $-\mu$. This gives the following difference equations for $c_\eta^\pm$:

$$n\varphi_1\,(\eta, \mu) + (1 - n)\, \varphi_1(\eta, -\mu) = 1, \tag{25a}$$

$$n\varphi_2\,(\eta, \mu) + (1 - n)\, \varphi_2(\eta, -\mu) = 1, \tag{25b}$$

where the concentration has been omitted as a common factor. Three cases can now be considered:

a) Purely ferromagnetic case, $n = 1$ or $n = 0$. The largest thermopower should occur here. The difference equations can be solved in an elementary way, however, the integrations to get I and W are very complicated.

b) Purely antiferromagnetic case, $n = 0.5$. For reasons of symmetry the thermopower vanishes; there is neither a difference between the elastic terms nor between the inelastic ones. However, the η-dependence of $c_\eta^\pm$ may influence the T-dependence of the resistivity. The difference equations cannot be solved in an elementary way.

c) Intermediate cases, $0.5 < n < 1$. Because the thermopower vanishes when $n = 0.5$ and because there is some preference in the literature for these cases it seems interesting to study the influence of small deviations from the antiferromagnetic case; the thermopower should remain anomalously high. Because the thermopower is insensitive to a sign reversal of μ and because the two factors favouring high values vanish if $n = 0.5$ a proportionality as $(n - 0.5)^2$ is expected for S as a first approximation.

3. *The computations.* Values of $I(\mu)$ and $W(\mu)$ for $\mu = 0.1 \times 2^i$, $i = 0\ (1)\ 7$, were calculated with the aid of the electronic computer Electrologica —X1 of the Mathematical Centre. This was done for the following 100 combinations of the parameters:

$$A = 1;\ C = 0.5,\ 0.25,\ 0.10;\ n = 1,\ 0.8,\ 0.52,\ 0.5;\ D = 0.2;$$

$$E = 0.25,\ 0.10,\ 0.05,\ 0,\ -0.10;\ S = 2.5\ (\text{except for } C = 0.5),\ 0.5.$$

To this end the difference equations (25) had to be solved for c_η^+ and c_η^-. The four boundary conditions required for the solution of this system were chosen in such a way as to give constant $c_\eta^\pm$ for $\eta = \pm\infty$. The values of these four constants were found by substitution of $\eta = \pm\infty$ into eq. (25) and solving the system thus obtained for $c_{\pm\infty}^+$ and $c_{\pm\infty}^-$.
By taking $\eta_l = \eta_0 + l\mu$, $l = 0(1)\ N$, in such a way that $\eta < \eta_0$ could be interpreted as $\eta = -\infty$ and $\eta > \eta_N$ as $\eta = \infty$, we arrived at two systems of $N + 1$ linear equations in the $2N + 2$ unknowns $c_{\eta_l}^\pm$, which were solved by an elimination procedure for tridiagonal matrices.

In order to obtain a table of $c_\eta^\pm$ with an increment sufficiently small to calculate the integrals (19) numerically, these computations had to be carried out for several values of η_0. In fact $\eta_0 = -(13 + 0.1\,j)$, $j = 0(1)10\mu - 1$ and $\eta_N \geq 13$ were chosen, thus finding values of $c_\eta^\pm$ for $\eta = -13(0.1)13$. Finally the integrals (19) were calculated, replacing the limits by ± 13, by means of the trapezoidal rule.

4. *Results.* The electrical resistivity. At *high* temperatures, $(\mu \to 0)$, $\overline{m} = 0$ for both fields and the resistivity does not depend on C.

Moreover, for $\kappa T \gg \Delta$ the inelastic character of the scattering disappears ($c_\eta \to c_0$); hence the resistivity must be identical with Yosida's result and independent of n. $\rho_\infty = A + (D - E)\, S(S+1)$, $T \gg \Delta/\kappa$.

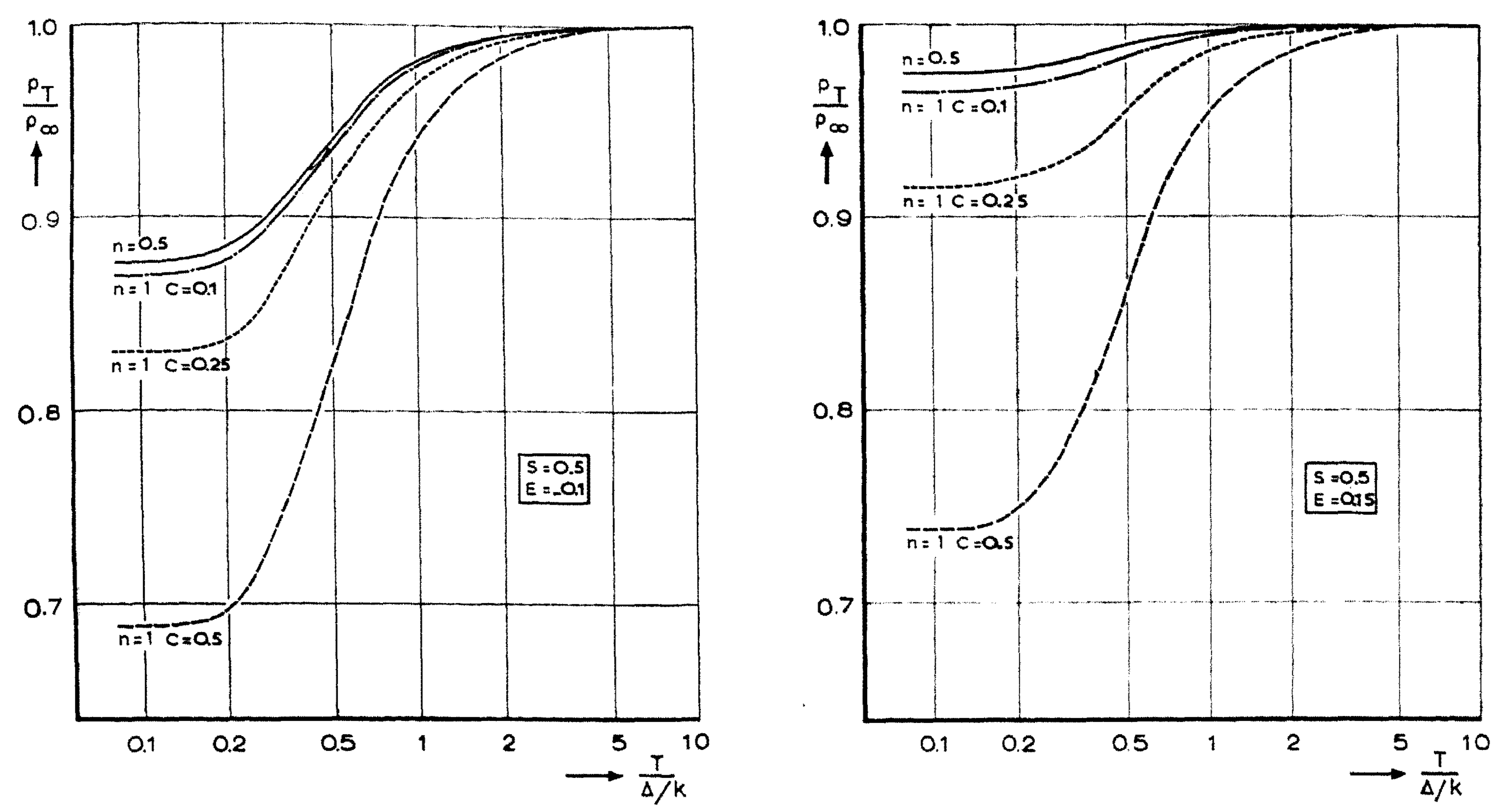

Fig. 1. The electrical resistivity as a function of the reduced temperature for a few values of the parameters. $S = 0.5$.
For $T \to \infty$ the resistivity does not depend on n and C.

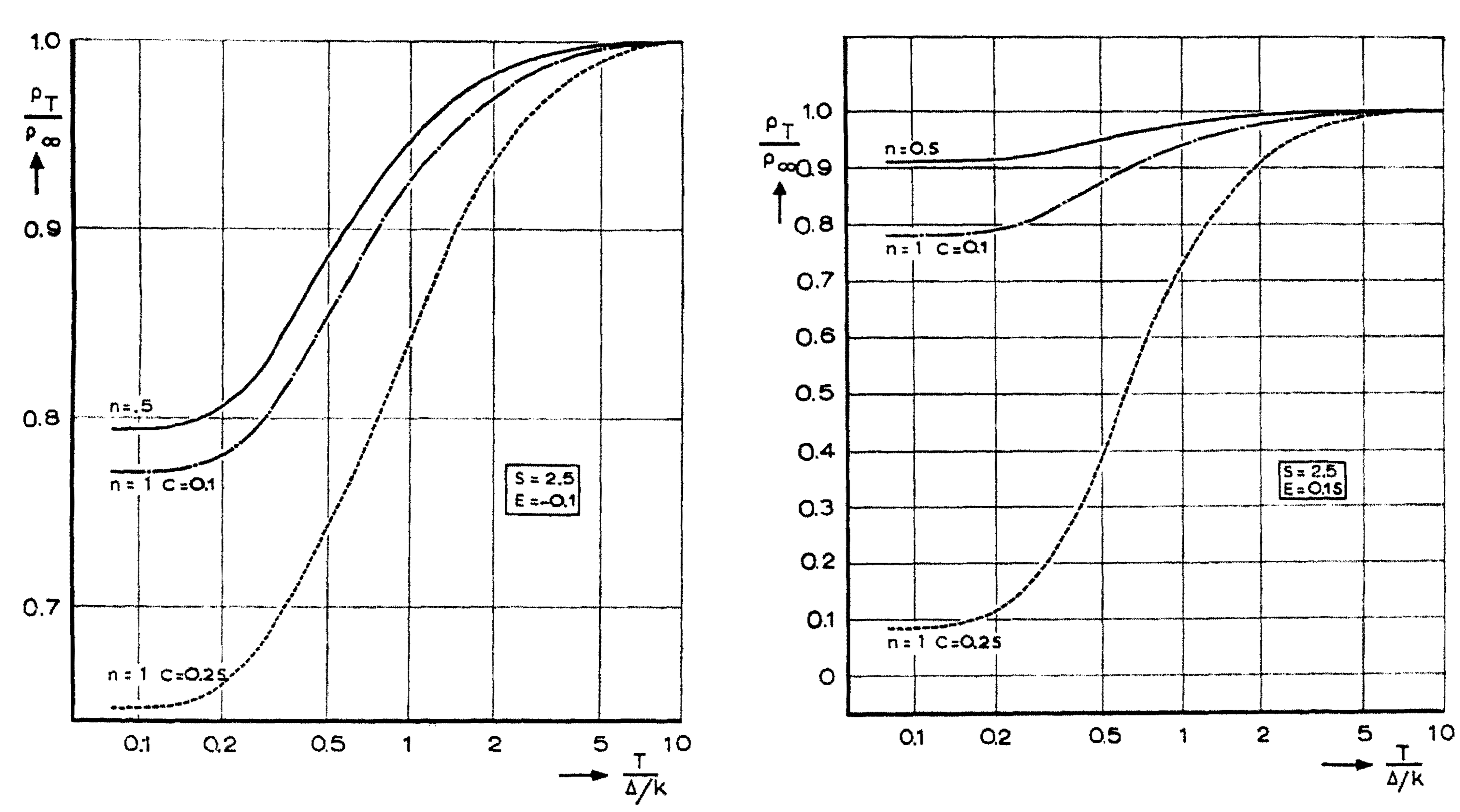

Fig. 2. As fig. 1 for $S = 2.5$.

Low temperatures ($\mu \to \infty, P \to 0$). For $n = 0.5$ the equations again simplify to Yosida's. The terms with C and $\overline{m}$ cancel because $n\overline{m}_\mu + (1-n)\,\overline{m}_{-\mu} \to 0$ and $\rho_0(0.5) = A + (D - E)\, S^2$, $\quad T \ll \Delta/\kappa$.

For the extreme ferromagnetic case $n = 1$

$$\rho_0(1) = \frac{\{A + (D - E)\, S^2\}^2 - 4C^2S^2}{A + (D - E)\, S^2}, \quad T \ll \Delta/\kappa.$$

It follows from these equations $\rho_\infty > \rho_0(0.5) > \rho_0(1)$.

Hence for all allowed values *) of D, E, C, S and n, the resistivity at $T = 0$ is lower than at high temperatures. Yosida found that this change takes place in a monotonic way. The possibility could not be excluded that by taking the η-dependence of the "relaxation-time" $c_\eta^\pm$ into account, the resistivity would pass through a maximum at intermediate temperatures. However the computations (some results are shown in figs. 1, 2) give only a slight modification of the Yosida result. It should be noted that 90% change in the resistivity takes place in a temperature range of about a factor 20.

The thermopower. Some of the computer results for S in units of $\kappa/e = 86.3\ \mu$V/degree are shown in fig. 3 and fig. 4. As the computation has been carried out for only a limited number of μ-values the interpolation is rather inaccurate especially at the lower temperatures where the thermopower falls extremely rapidly. At temperatures above the maximum, S goes to zero as T^{-2}, a result which is most probably valid beyond the details of our model. The maximum in S occurs for $T = \frac{1}{3}\Delta/\kappa$, approximately.

Neglecting extreme cases a maximum value of $0.1\ \kappa/e$ or about 10 μV/degree seems quite normal for cases where the change in resistivity is not too large, say 10 or 20%.

As expected, S is largest for $n = 1$ and vanishes for $n = 0.5$. The results for intermediate values of n, for which $n = 0.80$ and $n = 0.52$ have been chosen, are approximately proportional to $(n - 0.5)^2$. For $S = 0.5$ this holds remarkably well; for $S = 2.5$ the thermopower at $n = 0.52$ deviates by no more than a factor two from the value calculated with the above proportionality; at $n = 0.8$ the deviation is substantially smaller.

The above values of the thermopower increase in a monotonic way with increase of E between the extreme values $E = -0.10$ and $E = 0.15$, which are shown in figs. 3 and 4. For $S = 0.5$ the E dependence is quite weak.

An interesting result is that the thermopower is negative for positive C for all allowed values of the parameters. The thermopower is an odd function of C whereas the resistivity, the integral I, depends on the *absolute* value of C. These sign-reversal properties follow from the Boltzmann equation **).

5. *Discussion*. By taking the energy dependence of the relaxation-time into account results for the electrical resistivity were obtained which are

*) $D \geq E$; $A + (D - E)\, m^2 + 2Cm > 0$ for $-S \leq m \leq S$.

**) $e^{-\mu/2}\, P(\mu)$ is even in μ; $e^{\mu/2}\, Q(\eta, \mu) = Q'(\eta, \mu) = Q'(-\eta, -\mu)$; $c_\eta^+ + c_\eta^-$ is independent of the sign of μ.

not essentially different from the results in Yosida's simplified treatment [4]). The resulting monotonic decrease of the resistivity with decreasing T, as shown in figs. 1 and 2, has been observed in CuMn and AgMn [11]) alloys at higher concentrations. Neither the maximum in the resistivity of these alloys at lower concentrations, nor the monotonic increase with decreasing T of such alloys as CuFe, CuCo etc. [12]) resulted from our modified equations. It seems most unlikely that a distribution of internal fields could modify qualitatively the resistive behaviour in figs. 1 and 2. In this respect the influence of the finite life-time of the electrons due to inelastic collisions merits further research.

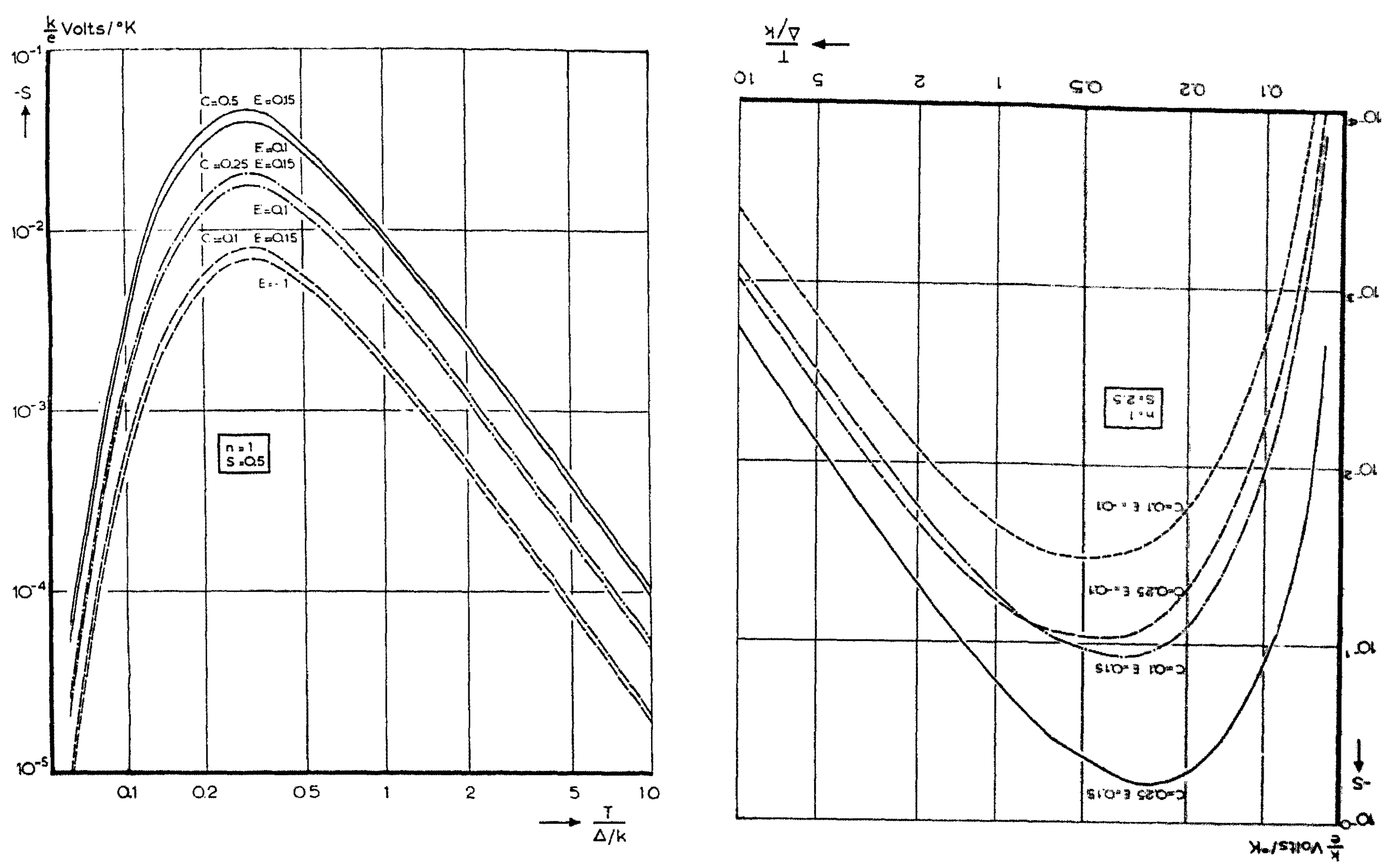

Fig. 3, 4. The thermopower in units of κ/e as a function of the reduced temperature. For $n = 0.5$ the thermopower vanishes exactly. fig. 3 corresponds with fig. 1; fig. 4 with fig. 2.

The calculated thermopower is of the order of the experimental values in cases where it is abnormally high and has, moreover, the correct sign if one assumes that the exchange integral, J, for electrons and ions is positive. Experimental data on thermopower are scarce. Fairly pure Cu, Ag and Au with possibly Fe as dominant impurity gave a thermopower of about -6μV/degree at 1°K. However our model cannot give the right resistive behaviour for this type of alloy.

The ion pair theories [6])[7]) seem to be able to predict all types of temperature dependence which have been observed for the resistive behaviour in magnetic dilute alloys but do not predict – at least not in the way in which these models have been worked out – anomalously high thermopower. In addition these theories predict a quadratic concentration dependence of the anomaly, which has not been observed experimentally. Brailsford and Overhauser [7]) consider isolated ions to account for a weaker concentration dependence. In this situation it is attractive to suppose that the ion pairs cause the anomalous T dependence of the resistivity and the "isolated" ions the giant thermopowers.

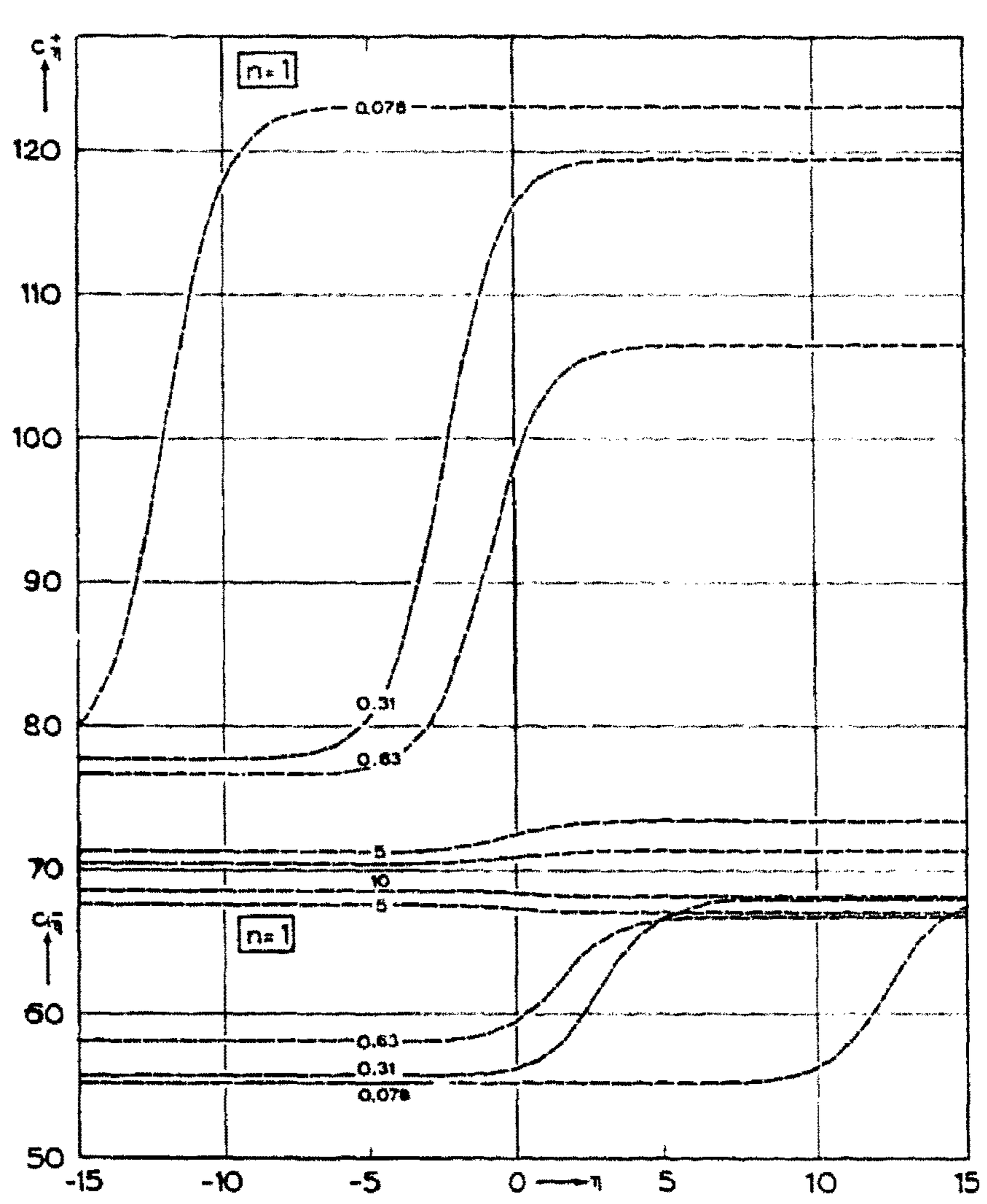

Fig. 5. The "relaxation times" c_η^+ and c_η^- as a function of η in the ferromagnetic case $n = 1$ for a few values of the reduced temperature, $\kappa T/\Delta$, for the parameter values $A = 1$, $D = 0.2$, $C = 0.1$, $E = 0.15$ and $S = 2.5$.

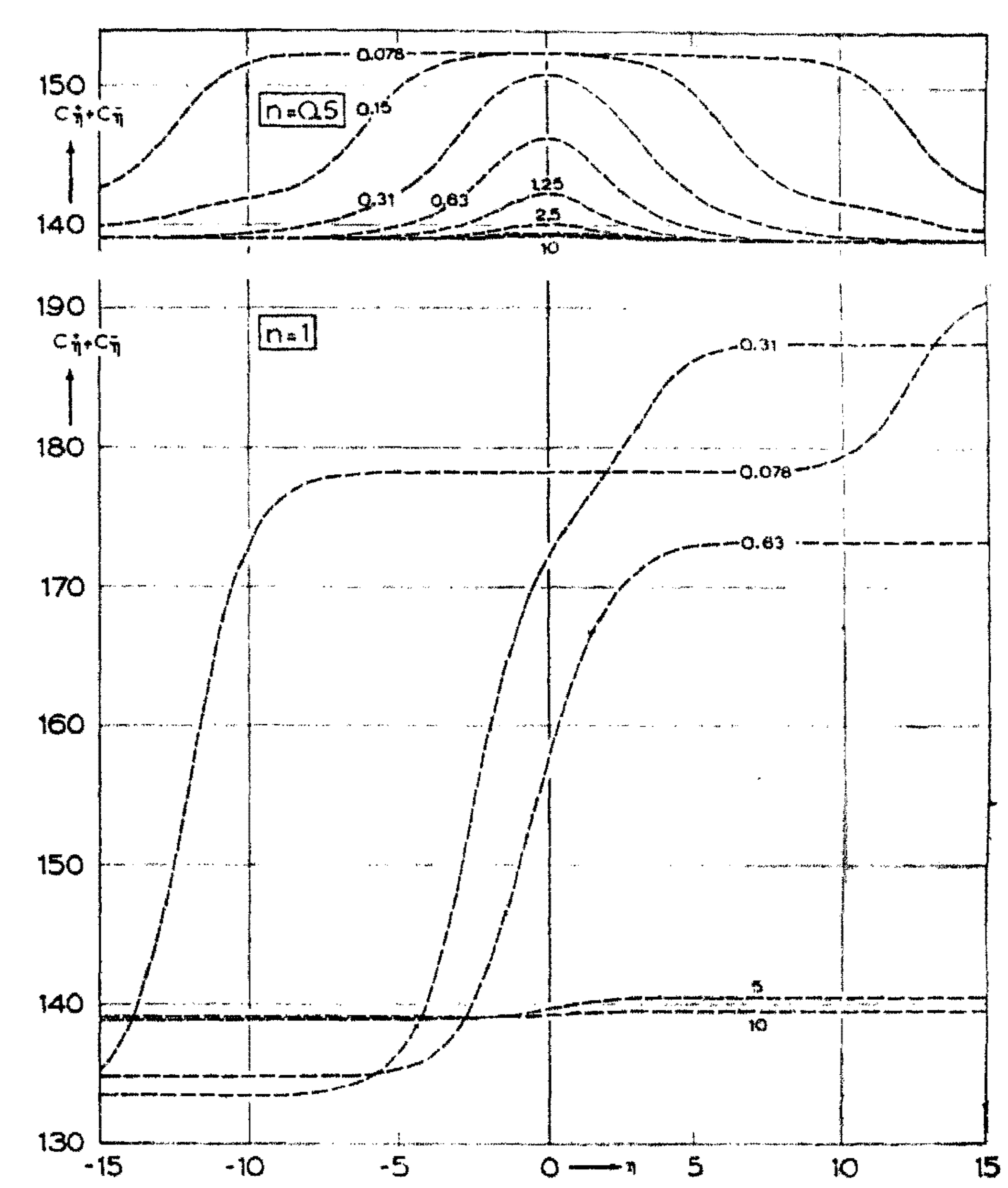

Fig. 6. The sum of the relaxation times $c_\eta^+ + c_\eta^-$ for the parameter values as in fig. 5. For $n = 0.5$ one has $c_\eta^+ = c_\eta^-$.

However, modifications similar to those introduced into Yosida's model in § 2 must also be applied to the ion pair calculations. These give undoubtedly a resistivity-temperature relation different from the one in the simplified treatments. As for the thermopower, the $\boldsymbol{S}.\boldsymbol{S}$ interaction between the members of an ion pair results in energy states which do not depend on the direction of the total magnetization, hence the pair scatters the electrons in such a way that there is on the average no difference between electrons with + and − spin. If one makes the energy of the pair dependent on the direction of the magnetic moment the scattering will become different for + and − spin electrons. This occurs in exactly the same manner as in the Yosida model, by interference between the normal and exchange parts of the elastic scattering. A first order thermopower approaching the value κ/e will again be the result. This removal of the spin degeneracy may be brought about by configurations of interacting pairs with or without isolated ions. The scarcity of the experimental data and the large number of such configurations make it inopportune to consider these possibilities in a more quantitative detail at present.

Appendix *). Fig. 5 shows the relaxation times c_η^+ and c_η^- for the parameter values $A = 1$, $D = 0.2$, $E = 0.15$, $C = 0.1$ and $S = 2.5$ for the ferromagnetic case, $n = 1$. Although only values close to $\eta = 0$ contribute to the integrals I and W, the values of $c_\eta^\pm$ in this region are determined by a much larger interval, especially for the higher μ-values. It was for this reason that variational principles were not used. These are based on a power development of $c_\eta^\pm$ around $\eta = 0$. As figs. 5 and 6 show such a procedure can not be expected to yield reliable results. Without elastic scattering ($P^\pm = 0$) one has in the ferromagnetic case $c_\eta^+ = c_{-\eta}^-$ so that if e.g. c_η^+ is a monotonically increasing function of η, c_η^- is monotonically decreasing. If the elastic scattering too is taken into account ($P^\pm \neq 0$) one is inclined to expect – by adding inverse relaxation times – that the sign of the above asymmetry for c_η^+ and c_η^- would remain the same. However, it is shown in fig. 5 that *both* c_η^+ and c_η^- are increasing with η for all but the highest values of $\kappa T/\Delta$. This points to the necessity of considering the elastic and inelastic scattering as an entirety. In fig. 6 the functions $c_\eta^+ + c_\eta^-$ are shown also for the antiferromagnetic case $n = 0.5$ for which $c_\eta^+ = c_\eta^- = \frac{1}{2}(c_\eta^+ + c_\eta^-)$. These functions have the same, η-independent, asymptotic value for $n = 1$ and $n = 0.5$ when $T \to \infty$. We note that for $n = 1$ the "mean relaxation time" $c_\eta^+ + c_\eta^-$ is not everywhere a monotonic function of the temperature.

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*) This appendix was written after we became informed about similar work of Bailyn (to be published) and about a related discussion by Guénault and MacDonald (to be published). We thank these authors for sending us preprints of their work.

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