Vol. A42 (1972) ACTA PHYSICA POLONICA No 5

INFLUENCE OF INTERACTIONS BETWEEN LOCALIZED MAGNETIC MOMENTS ON THE THERMOELECTRIC POWER OF DILUTE MAGNETIC ALLOYS

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(Received August 14, 1971)

Short range magnetic coupling occurs in many dilute solid solution of ferromagnetic transition elements in gold and copper [1, 2]. The effect of this ferromagnetic coupling on the thermoelectric power is investigated on the basis of the modified *s-d* exchange model. The exchange type interaction between the localized magnetic moments are included. It is found that in the effect of the ferromagnetic coupling or antiferromagnetic coupling the anomalous term in the thermoelectric power is strongly reduced. Therefore, these simple consideration may prove useful when describing the thermoelectric power of dilute magnetic alloys of the AuFe type at concentration of the magnetic atoms not low enough for the interaction between the impurities to be negligible. On the basis of the present paper it is possible to make a theoretical interpretation of the measurements of Mac Donald, Pearson and Templeton *(Proc. Roy. Soc.*, **A266**, 161 (1963).

1. Introduction

Progress in the theory of transport phenomena in very dilute magnetic alloys was first made when Kondo [3, 4, 5] attempted to explain the resistivity minimum in such materials [3]. In recent times enormous efforts have been expended on both experimental and theoretical researches on very dilute alloys consisting of noble metals with isolated magnetic atoms of the 3d group [6, 7, 8, 9]. Earlier knowledge of the effect of the magnetic coupling of the magnetic atoms on the properties of these alloys was relatively scarce. On the other hand, the short-order interactions between localized magnetic moments were found experimentally by many authors [1, 2, 10, 11]. Gerritsen [10] found a consistent indication of a transition temperature in several AuFe alloys containing more than 0.15% Fe in solution. The idea of the existence of superparamagnetic regions in AuFe alloys is also supported by the magnetization measurements of Tournier and Ishikawa [11]

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down to temperatures of the order of 0.05°K and in fields up to 25 kOe. They conclude that the magnetization field curves in the alloy containing 8 % Fe are consistent with there being an array of superparamagnetic particles. Mac Donald, Pearson and Templeton made thermoelectric power observations in dilute magnetic AuFe alloys. They found that the magnitude of the thermoelectric power decreases when the concentration of the impurity atoms increases. This fact has found any theoretical explanation on the basis of the model of isolated magnetic impurities. Therefore, we believe, our work may help to interpret the thermoelectric power of the AuFe alloys when the concentration of iron atoms is not small enough to be able to neglect the interactions between the magnetic atoms. Namely, we found that in the effect of the parallel or antiparallel coupling of the localized magnetic moments the thermoelectric power is strongly reduced, especially in the low temperature region. Preliminary results have been recently published [12]. It is, of course, quite obvious that our results are only of a qualitative nature, this attempt to calculate the thermoelectric power of a system having coupled magnetic moments is rather tentative. Actually, we calculate here the thermoelectric power due to scattering of conduction electrons by one pair of interacting impurities in the following approach: we adopt the $s-d$ exchange model, and assume the conduction electrons to be free and the two impurities with spin operators S_1 and S_2, respectively, to be coupled by an effective exchange interaction J_1.

2. *Calculations of the thermoelectric power*

In the second quantization representation the Hamiltonian of a system of free electrons and coupled pairs of localized spins takes the following form:

$$H_0 = \sum_{k,s} E_k a^+_{k,s} a_{k,s} - J_1 \vec{S}_1 \cdot \vec{S}_2 - 2\mu_B \vec{H} \cdot (\vec{S}_1 + \vec{S}_2), \tag{1}$$

where $a^+_{k,s}$, $a_{k,s}$ are the creation and annihilation operators of a conduction electron in the one electron state $|k, s\rangle$ with momentum k, spin s and energy E_k. H is the effective magnetic field acting on the magnetic moments localized around the impurity atoms. $\vec{S}_1$ and $\vec{S}_2$ denote the spin operators of the first and second impurity atom, respectively. The term describing the exchange type coupling between the spins of the magnetic atoms satisfies the following eigenvalue equation:

$$-2J_1 S_1 S_2 |m, S\rangle = -J_1[S(S+1)+2S'(S'+1)]|\, m, S\rangle \tag{2}$$

where S' is the value of the spin of one impurity atom and S denotes the total spin of the pair of impurities taking on values of 0, 1, 2, 3, ... 2S'.

The perturbing Hamiltonian is given as

$$H' = -\frac{2J}{N} \sum_{\substack{\vec{k},s \\ \vec{k}',s'}} (\vec{S}_1 + \vec{S}_2) \cdot \vec{\sigma}_{s,s'} a^+_{k,s} a_{k',s'} + V a^+_{k,s} a_{k's'}, \tag{3}$$

where the vectors $\vec{\sigma}_{s,s'}$, have the following components:

$$\vec{\sigma}_{++} \equiv (0, 0, \tfrac{1}{2})$$

$$\vec{\sigma}_{--} \equiv (0, 0, -\tfrac{1}{2})$$

$$\vec{\sigma}_{+-} \equiv \left(\frac{1}{2}, -\frac{i}{2}, 0\right)$$

$$\vec{\sigma}_{-+} \equiv \left(\frac{1}{2}, \frac{i}{2}, 0\right) \tag{4}$$

V denotes the impurity potential, which involves the difference of the valence, the redistribution of the conduction electrons around the impurity and the lattice distortion around it. We shall now calculate the thermoelectric power in the system described by the sum of (1) and (3). Generally, the thermoelectric power is expressed by the following formula:

$$P = \frac{\int \tau_k(E_k) \frac{df_k^0}{dE_k} V_{\vec{k}}^2 \varrho(E_k) E_k dE_k}{-eT \int \tau_k(E_k) \frac{df_k^0}{dE_k} V_k^2 \varrho(E_k) dE_k} \tag{5}$$

where $v_k = hk/m$, and the energy of the conduction band is measured from the Fermi surface. f_k^0 is the Fermi distribution function. The relaxation time $\tau_{\vec{k}}$ is defined as

$$\frac{1}{\tau_k} = \sum_{k'} [W(\vec{k}_\pm \to \vec{k}'_\pm) + W(\vec{k}_\pm \to \vec{k}'_\pm)], \tag{6}$$

where the transition probability per unit time of the process in which the electron goes from the initial state $|k, s\rangle$ to the final state $|k', s'\rangle$, $W(\vec{k}, s\ \vec{k}', s')$ is given to the second Born approximation as

$$W(a \to b) = \frac{2\pi}{\hbar} \delta(E_a - E_b) \left| H'_{ba} + \sum_{c=a} \frac{H'_{bc} H'_{ca}}{E_a - E_c + is} \right|^2 \tag{7}$$

where $|a\rangle$ and $|b\rangle$ are unperturbed states of the itinerant electrons and interacting localized spins of the impurity atoms with an occupied and empty one-electron state $|k, s\rangle$ respectively. E_a, E_b and E_c denote the energies of the unperturbed system in these states. In the second quantization notation each unperturbed state $|l\rangle$ can be expressed in the following form:

$$|l\rangle \equiv \prod_{\vec{k}j} (\overset{+}{a}_{kj+})^{n_{kj+}} (\overset{+}{a}_{kj-})^{n_{kj-}} \ldots |0\rangle |S, m\rangle, \tag{8}$$

where $n_{k_j,s}$ are the occupation numbers of the one-electron state $|k_j, s\rangle \cdot S = 0, 1, 2, \ldots 2S'$ is the value of the spin of the pair of the magnetic moments. We assume that each impurity atom has spin equal S', m denotes the possible values of the z component of the total spin of the pair of localized magnetic moments and for a given S can be equal to $-S$, $-S+1$, $-S+2$, ... S. The vacuum state $|0\rangle$ is defined by the quality

$$\overset{+}{a}_{k_j s}|0\rangle \equiv 0|0\rangle \equiv 0. \tag{9}$$

The spin dependent part of the perturbing Hamiltonian (3) satisfies the following equations:

$$\begin{aligned}
\vec{S}\cdot\vec{\sigma}_{++}|S, m\rangle &= \tfrac{1}{2}\, m|S, m\rangle,\\
\vec{S}\cdot\vec{\sigma}_{--}\,|S, m\rangle &= -\tfrac{1}{2}\, m|S, m\rangle,\\
\vec{S}\cdot\sigma_{+-}|S, m\rangle &= \tfrac{1}{2}\,[(S+m)(S-m+1)]^{\frac{1}{2}}\,|S, m-1\rangle,\\
\vec{S}\cdot\sigma_{-+}|S, m\rangle &= \tfrac{1}{2}\,[(S+m+1)(S-m)]^{\frac{1}{2}}|S, m+1\rangle
\end{aligned} \tag{10}$$

where $\vec{S} = \vec{S}_1+\vec{S}_2$ is the operator of the spin of the interacting magnetic impurities.

Using the relations (3), (8), (9) and (10) we can easily prove that, except for the case of transitions of the systems between the unperturbed states $|a\rangle$ and $|b\rangle$ in which only the one electron states $|k, s\rangle$ and $|k', s'\rangle$ have the different occupation numbers, the perturbing Hamiltonian (3) provides zero matrix elements. Let us consider, for example, an element of the type:

$$-\frac{J}{N}\langle m, S|\langle 0|(a_{k'-})^0 \ldots (a_{k+})^1 \ldots (a_{k_i,s_i})^{n_{k,\,si}} \sum_{\vec{k}_1,\vec{k}_2} (\vec{\sigma}_{+-}\cdot\vec{S})\overset{+}{a}_{k_2+}a_{k_1-}\,(\overset{+}{a}_{k,si})^{n'_{ki,si}} \ldots$$

$$\ldots (a_{k+})^0 \ldots (\overset{+}{a}_{k'-})^1 \ldots |0\rangle|m', S''\rangle. \tag{11}$$

Expression (11) provides a non zero contribution only if:

1. $k_{2+} = k_+$ because, when this condition is not satisfied the destruction operator a_{k+} acts on the vacuum state and from (9) $a_{k+}|0\rangle = 0$. (This can be proved by considering some displacements of a_{k-} in (11).)

2. $k_{1-} = k'_-$ and $n_{k_i,s_i} = n'_{k_i,s_i}$. This condition can be proved on the same way as in 1.

3. $S'' = S$, $m' = m+1$. This is obtained from (10) and the orthogonality of the spin part of the wave functions (8).

These considerations show us that non-zero matrix elements of the (11) type occur for the following processes:

$$|a\rangle \equiv |(\overset{+}{a}_{k_i's_i})^{n_{ki,si}} \ldots (\overset{+}{a}_{k-})^1 \ldots (\overset{+}{a}_{k'-})^0 \ldots |0\rangle|S, m\rangle \rightarrow$$

$$\rightarrow |b\rangle \equiv |(\overset{+}{a}_{k_i's_i})^{n_{ki,si}} \ldots (\overset{+}{a}_{k-})^0 \ldots (\overset{+}{a}_{k'-})^1 \ldots |0\rangle|S, m-1\rangle \tag{12}$$

where

$$H_{ba'} = -\frac{J}{N}[(S+m)(S-m+1)]^{\frac{1}{2}} \tag{13}$$

In general, there exists only three types of transition in which a conduction electron is scattered from the initial state $|k+\rangle$ to the final state $|k'+\rangle$.

These processes can be described as:

$$|a\rangle \equiv |(a^+_{k+})^1 \dots (a^+_{k'+})^0 \dots |0\rangle|S, m\rangle \rightarrow$$

$$\rightarrow |b\rangle \equiv |(a^+_{k+})^0 \dots (a^+_{k'+})^1 \dots |0\rangle|S, m\rangle \tag{14}$$

with

$$E_a - E_b = E_k - E_{k'},$$

$$|a\rangle \equiv |(a^+_{k+})^1 \dots (a^+_{q-})^0 \dots (a^+_{k'+})^0 \dots |0\rangle|S, m\rangle \rightarrow$$

$$\rightarrow |c\rangle \equiv |(a^+_{k+})^0 \dots (a^+_{q-})^1 \dots (a^+_{k'+})^0 \dots |0\rangle|S, m+1\rangle \rightarrow$$

$$\rightarrow |b\rangle \equiv |(a^+_{k+})^0 \dots (a^+_{q-})^0 (a^+_{k'+})^1 \dots |0\rangle|S, m\rangle, \tag{15}$$

$$|a\rangle \equiv |(a^+_{k+})^1 \dots (a^+_{q-})^1 \dots (a^+_{k'+})^0 \dots |0\rangle|S, m\rangle \rightarrow$$

$$\rightarrow |c\rangle \equiv |(a^+_{k+})^0 \dots (a^+_{q-})^0 \dots (a_{k'+})^1 \dots |0\rangle|S, m-1\rangle \rightarrow$$

$$\rightarrow |b\rangle \equiv |(a_{k+})^0 \dots (a^+_{q-})^1 \dots (a^+_{k'+})^1 \dots |0\rangle|S, m\rangle. \tag{16}$$

Calculation of the transition probability, relaxation time and the thermoelectric power on the basis of (6), (7), (8) and (12)–(15) is straightforward as has been shown elsewhere [3, 4, 5]. After some lenghty but simple calculations we obtain that the thermoelectric power, P is given as

$$P = \frac{2\dfrac{k}{e}\displaystyle\sum_{s=0}^{2S'} A(S)p(S)}{2V^2 + \displaystyle\sum_{s=0}^{2s'} B(S)p(S)}, \tag{17}$$

where

$$p(S) = \frac{\exp \dfrac{J_1}{kT} S(S+1)}{\displaystyle\sum_{s=0}^{2s'} \sum_{m=-s}^{+s} \exp \dfrac{J_1}{kT} S(S+1)}, \tag{18}$$

$$B(S) = J^2 S(S+1). \tag{19}$$

Let us now examine the behaviour of the giant thermoelectric power in the regions of low and high temperatures, respectively. In the low temperature limit, *i. e.* when $\mu_B H \gg kT$ the function $A(S)$ takes the following form:

$$A(S) = 4\pi^2 \varrho^2 V J^3 S^2 \left(\frac{\mu_B H}{kT}\right)^2 \exp \frac{-2\mu_B H}{kT}. \tag{20}$$

For the high temperatures, when $\mu_B H \ll kT$ we have

$$A(S) = 4\pi^2 \varrho^2 V J^3 S(S+1)\left[1 - \frac{5}{9}\left(\frac{\mu_B H}{kT}\right)^2\right]. \tag{21}$$

Let us compare the results of formula (17) with Kondo's thermoelectric power for noninteracting magnetic impurities. In the low temperatures the giant thermoelectric power obtained by Kondo is expressed by

$$P_K = \frac{16\pi^2 \varrho^2 V J^3 \frac{k}{e} S'^2 \left(\frac{\mu_B H}{kT}\right)^2 \exp \frac{-2\mu_B H}{kT}}{V^2 + J^2 S'(S'+1)}. \tag{22}$$

Therefore, the ratio of (17) for the ferromagnetic coupling to the Kondo's result in the low temperature limit is

$$\frac{P_{\uparrow\uparrow}}{P_K} = \frac{2V^2 + J^2 S(S+1)}{(4S+1)V^2 + J^2 S(2S+1)}. \tag{23}$$

For $S = 2$ the value of $J^2 S(S+1)/2V^2$ is equal approximately to 0.01 [3], [4]. Therefore, for this spin we have

$$\frac{P_{\uparrow\uparrow}}{P_K} = 0.28. \tag{24}$$

At the other extreme, *i. e.*, for $J_1 \ll kT$ and moreover $\mu_B H \ll kT$, the pair of interacting magnetic moments acts on conduction electrons as two free spins; thus from formula (17) we obtain the Kondo giant thermoelectric power. A more exact numerical discussion

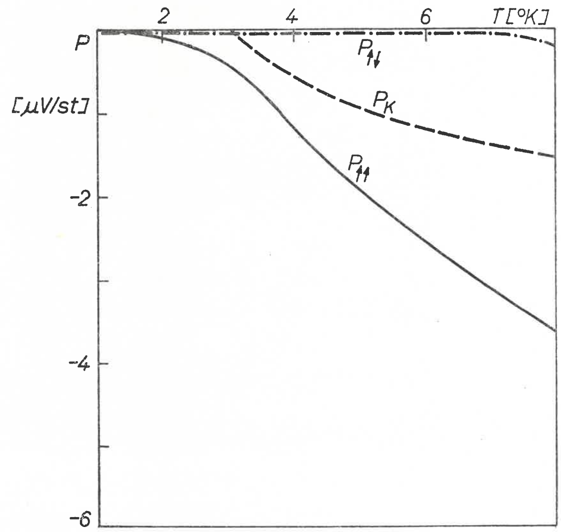

Fig. 1. Comparison of the numerical results of the present paper with Kondo's giant thermoelectric power for noninteracting magnetic impurities for $S = \frac{1}{2}$. $P_{\uparrow\uparrow}$, $P_{\uparrow\downarrow}$ denote the thermoelectric power for parallel and antiparallel magnetic coupling, respectively. P_K — is the curve obtained by Kondo

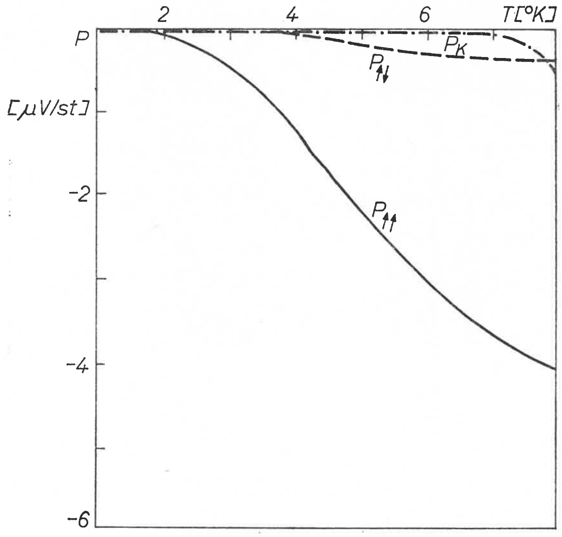

Fig. 2. Thermoelectric power for $S = 1$

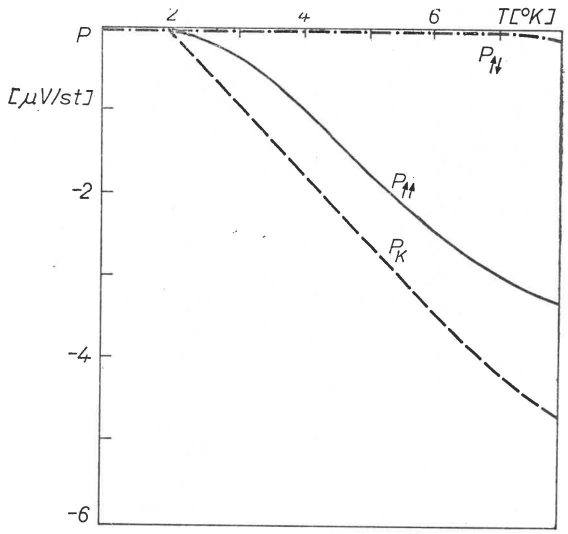

Fig. 3. Thermoelectric power for $S = \frac{3}{2}$

of the dependence of the thermoelectric power on temperature for both types of magnetic coupling is shown in Figs 1 to 8. In these figures we take $\dfrac{2\pi^2\varrho^2J^2}{V} = 0.33$ [4]. The exchange coupling parameter corresponds to the Curie temperature of the $Au_{0.86}Fe_{0.14}$ alloy, *i. e.* 104°K. As seen in the Figs 1 to 8, the thermoelectric power due to a pair of interacting localized magnetic moments is generally smaller than Kondo thermoelectric power of isolated magnetic impurities. On the other hand, for parallel coupling and very high temperatures, *i. e.* for $J_1 \ll kT$, we have $P_{\uparrow\uparrow} = P_K$.

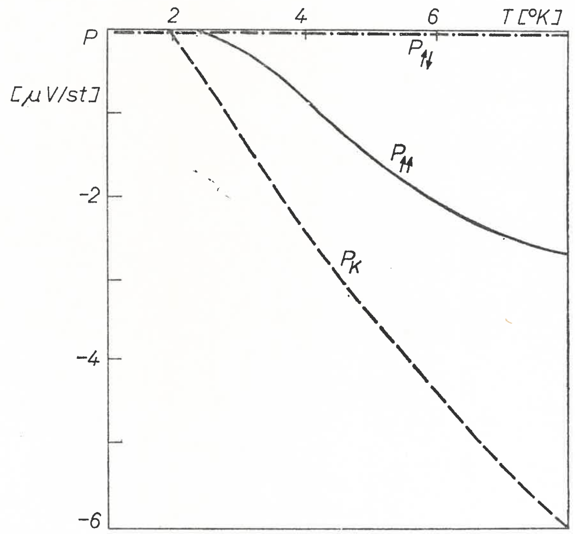

Fig. 4. Thermoelectric power for $S = 2$ (this value of localized spin does occur in most AuFe and CuFe alloys)

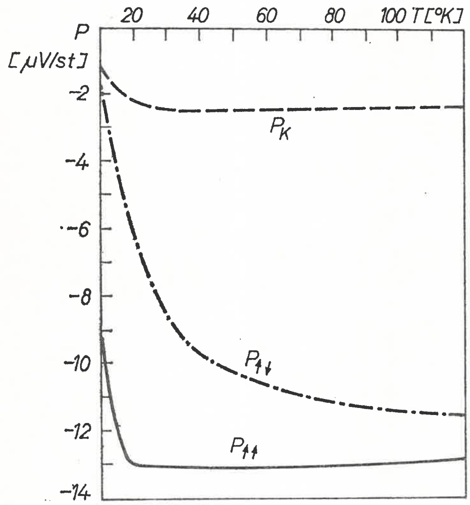

Fig. 5

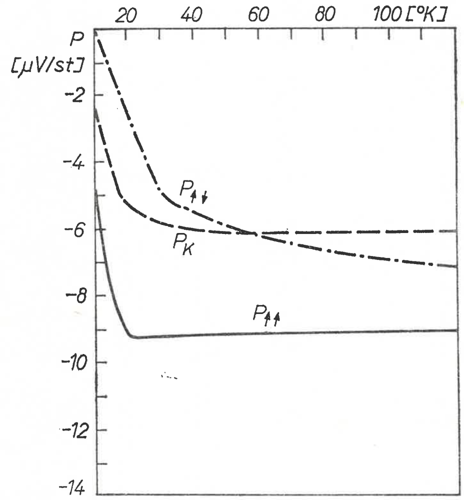

Fig. 6

Fig. 5. Thermoelectric power for $S = \frac{1}{2}$ at the higher temperatures
Fig. 6. Thermoelectric power for $S = 1$ in the high temperatures region

Let us now investigate the effect of antiferromagnetic coupling on thermoelectric power. In the low temperature limit we have

$$\frac{P_{\uparrow\downarrow}}{P_K} = \frac{V^2 + 3J^2}{V^2 \times \exp\left(\frac{J_1}{kT}\right) - \frac{J^2}{4}} \tag{25}$$

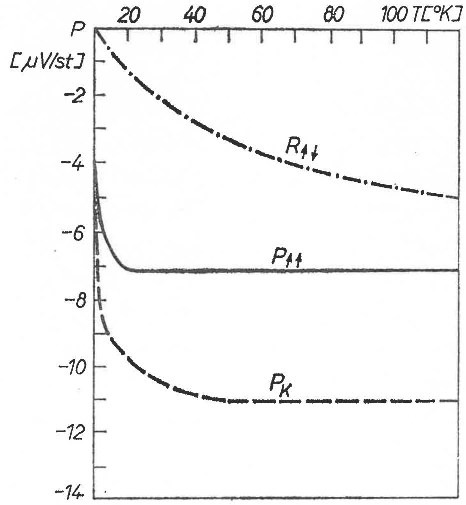

Fig. 7. Thermoelectric power for $S = \frac{3}{2}$

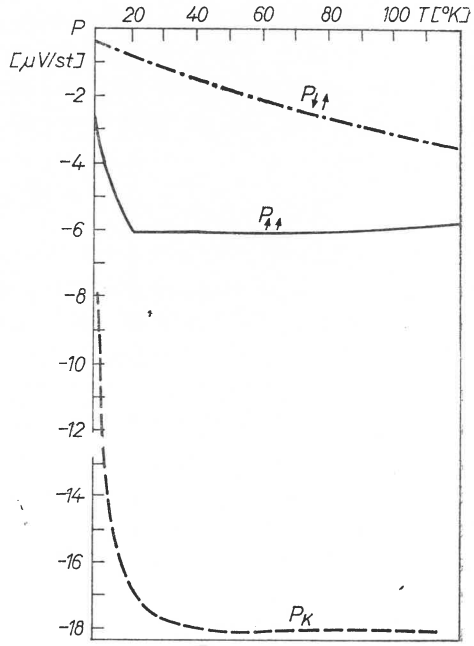

Fig. 8. Thermoelectric power for $S = 2$

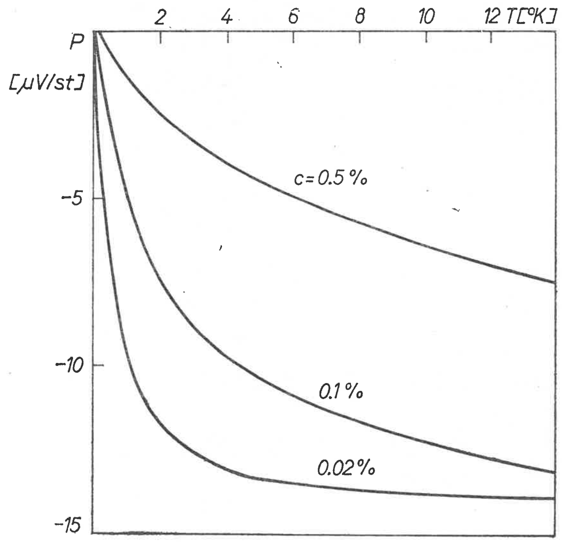

Fig. 9. The results of measurements by Mac Donald, Pearson and Templeton [13]

The formula (25) implies that at the low temperatures conduction electrons "feel" the total spin of the pair of magnetic atoms, which is equal to zero. Hence, there is no scattering of conduction electrons. Note that our theoretical conclusions agree quite well with the measurements of thermoelectric power for AuFe alloys performed by Mac Donald, Pearson and Templeton [13]. They suggest that the thermoelectric power decreases when the concentration of the impurity atoms increases, *i. e.* when the coupling between the localized magnetic moments becomes more and more important. The results of the measurements of Mac Donald, Pearson and Templeton are shown in Fig. 9.

3. Conclusions

Experimental investigations of the influence of magnetic coupling on the phenomena occurring in dilute magnetic alloys are currently at stage of rapid development. On the other hand, nearly all detailed theoretical calculations dealing with the low-temperature behaviour of the electrical resistivity and thermoelectric power commence from the model of isolated magnetic impurities. The magnetic interactions are neglected. This paper is a tentative attempt to investigate the effect of coupling on the transport phenomena encountered in dilute magnetic alloys. We present a calculation of the thermoelectric power due to scattering of conduction electrons by one pair of interacting magnetic impurities, using the modified Kondo Hamiltonian. Account is taken of the exchange interactions between the localized magnetic moments. We find that magnetic coupling strongly reduced the thermoelectric power, especially at the low temperatures. This reduction is greater for the antiferromagnetic coupling. In the case of high temperatures we obtain the results of Kondo for isolated impurity atoms. We believe that our simple procedure may be useful when describing the thermoelectric power of dilute magnetic alloys of the AuFe type at impurity concentration not low enough to be able to neglect the magnetic interactions between the impurity atoms.

The author's thanks are due to Professor J. Morkowski for calling this problem to his attention and many valuable discussions.

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