

## THERMOELECTRIC POWER IN SPINEL FERRITES\*

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The effect of exchange interactions on the thermoelectric power of the spinel ferrites has been discussed by means of a simple model of a  $s-d$  exchange interaction. A comparison of our results with the experimental data suggests a hopping mechanism of an electron transport in those compounds and allows one to determine the sign and to estimate the magnitude of the  $s-d$  exchange interaction integral.

## 1. Introduction

In the present decade, considerable interest has been devoted to the study of the electronic transport phenomena in ferrites [1-3]. Because of the well known difficulties connected with Hall constant measurements, many experiments were devoted to measuring the thermoelectric power. The aim of studying the thermoelectric power was to find what the transport mechanisms are like in the substances under consideration. Ferrites belong to a class of magnetic semiconductors with low mobility ( $\mu_0 \approx 1 \text{ cm}^2/\text{Vs}$ ) of both drift and Hall electric current carriers.

Usually the data from thermoelectric power experiments are interpreted in terms of two different transport mechanisms — thermally activated hopping (see e.g. [1, 2]) and standard band mechanism (see e.g. [3]) with polarons as electric charge carriers. The effect of the magnetic ordering of the compounds of our interest on the thermoelectric power has not been taken into account so far. In [2], the authors assumed the splitting of transport energy levels, of iron ions in the  $B$  sublattice, extending thus Jonker's single band hopping model [6, 15] to a two-energy-level model and obtaining a satisfactory agreement with the experimental results.

In paper [16] a hopping model, with small polarons as electric current carriers, was used to discuss the Hall effect in nickel ferrites and shown to explain results of the paper [3].

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In the present paper the effect of exchange interactions on the thermoelectric power is discussed and a comparison of the obtained results with experimental data is made. It is shown that taking into account the exchange interactions one is lead, in a natural way, to the Griffiths, Elwell and Parker model [2]. Moreover, it is shown that there is a possibility of estimating the  $s$ - $d$  exchange interaction integral and of determining a temperature dependence of the energy gap due to exchange interactions.

## 2. Model and Hamiltonian of the system

In paper [4] a simple model of a narrow energy band nondegenerate ferromagnetic semiconductor was discussed. Motion of an electric current carrier, described by a Wannier wave function takes place in an ionic lattice so we shall take into account its interaction with lattice oscillations. As a result of this interaction an electrostatic polaron<sup>1</sup> is formed. The interaction of the polaron with magnetic moments localized in lattice sites will be described by a model with a contact  $s$ - $d$  interaction.

The Hamiltonian of our model has the form

$$H = H_{el} + H_{ph} + H_{eph} + H_{dd} + H_{sd}, \quad (2.1)$$

where

$$H_{el} = \sum_{f,\sigma} [\varepsilon a_{f\sigma}^+ a_{f\sigma} - \sum_m V(\mathbf{m}) a_{f+m,\sigma}^+ a_{f\sigma}] \quad (2.2)$$

describes the energy of an electron in a periodic field of the crystalline lattice. Oscillations of the lattice, in a harmonic approximation, are given by

$$H_{ph} = \sum_q \hbar \omega_q (b_q^+ b_q + \frac{1}{2}). \quad (2.3)$$

A term, of the Hamiltonian, describing electron-phonon interaction, is written as follows

$$H_{eph} = \sum_{f,q,\sigma} \hbar \omega_q (\gamma_{fq}^* b_q + \text{h.c.}) a_{f\sigma}^+ a_{f\sigma}. \quad (2.4)$$

The last two terms in (2.1) have the form:

$$H_{dd} = -2I \sum_{f,m} S_f \cdot S_{f+m}, \quad (2.5)$$

$$H_{sd} = -2A \sum_f S_f \cdot \sigma_f. \quad (2.6)$$

$H_{dd}$  describes the interaction among the localized magnetic moments,  $a_{f\sigma}^+(b_q^+)$  is an electron (phonon) creation operator in a state  $f\sigma$  ( $q$ );  $q = \mathbf{q}, j$  ( $j$  — label longitudinal branches of a phonon spectrum),  $V(\mathbf{m})$  — the resonance integral,  $\mathbf{m}$  — the vector to the nearest neighbours.  $S_f$  — the operator of a spin localized in an  $f$ -th site,  $I(A)$  — the  $d$ - $d$  ( $s$ - $d$ ) exchange integral.

The expressions (2.2) and (2.5) are written in the nearest neighbour approximation and the crystalline lattice will be assumed cubic.

<sup>1</sup> The  $s$ - $d$  interaction alone cannot lead to a formation of the polaron state when  $T \ll T_C$  [4b, c].

Diagonalisation of the Hamiltonian (2.1) will be carried out by means of a canonical and unitary transformation. We write

$$\tilde{H} = T_{\text{ex}} T_{\text{ph}} H T_{\text{ph}}^+ T_{\text{ex}}^+ = H_e + H_b, \quad (2.7)$$

$$T_{\text{ex(ph)}} = \exp [U_{\text{ex(ph)}}]. \quad (2.8)$$

With  $2|\langle S^z \rangle| > 1$  and  $z|I| < |A|$  we find

$$U_{\text{ex}} = -\frac{1}{2} \sum_f [\hat{\Phi}_f S_f^+ \sigma^- + \text{h.c.}], \quad (2.9)$$

$$\hat{\Phi}_f = (1 + \sigma^z - S_f^z)^{-1}.$$

$$U_{\text{ph}} = \sum_{f,q,\sigma} (\gamma_{fq} b_q^+ - \text{h.c.}) a_{f\sigma}^+ a_{f\sigma}, \quad \text{with} \quad (2.10)$$

$$\gamma_{fq} = \frac{1}{\sqrt{N}} \frac{V_q}{\hbar \omega_q} \exp(iq \cdot f).$$

$2N$  denotes the number of sites in a system,  $V_q$  — an electron-lattice interaction parameter.

The terms  $H$ , due to a carrier, have been included in the Hamiltonian  $H_e$ , and terms due to the lattice and the localized spin system — to  $H_b$ . From now on, we shall be interested only in the kinetics of a carrier described by  $H_e$ . Neglecting the interaction among the carriers, we have

$$H_e = \sum_{f,\sigma} \varepsilon_\sigma a_{f\sigma}^+ a_{f\sigma} + H_1, \quad (2.11)$$

$$H_1 = -T_{\text{ex}} T_{\text{ph}} \sum_{f,m,\sigma} V(m) a_{f+m,\sigma}^+ a_{f\sigma} T_{\text{ph}}^+ T_{\text{ex}}^+, \quad (2.12)$$

$$\varepsilon_\sigma = \varepsilon^{(1)} - \varepsilon_m(\sigma) = \varepsilon^{(1)} - A \left\langle \frac{S(S+1) + (S^z)^2}{1 + 4\sigma S^z} \right\rangle, \quad (2.13)$$

$$\varepsilon^{(1)} = \varepsilon - \varepsilon_p, \quad \varepsilon_p = \sum_q \hbar \omega_q |\gamma_q|^2; \quad \sigma = \pm \frac{1}{2},$$

$$\langle \dots \rangle = \text{Tr} (e^{-\beta \tilde{H}} \dots) / \text{Tr} e^{-\beta \tilde{H}},$$

$\varepsilon_p$  — is the polaron binding energy. The last term in (2.13) describes a carrier energy change caused by its exchange interaction with the localized spins.

### 3. Thermoelectric power of a ferromagnetic semiconductor

Let the system under consideration be placed in an external static electric field  $E$  and temperature gradient. Then, according to the phenomenological transport theory, the electric current density  $J$  and the energy flux density  $Q$  are linear functions of the electrochemical potential gradient  $\mu$  and of the temperature;

$$J = L_1 \left( E + \frac{T}{e} \text{grad } \xi \right) - L_2 \frac{\text{grad } T}{T}, \quad (3.1)$$

$$Q = L_3 \left( E + \frac{T}{e} \text{grad } \xi \right) - L_4 \frac{\text{grad } T}{T}, \quad (3.2)$$

where  $\xi = \zeta/T$ ,  $\mu = \zeta - e\varphi$ ;  $\zeta$  — is the chemical potential,  $(-e)$  — an electron charge. From (3.1) and (3.2) we get

$$E = \rho J + \varphi \text{ grad } T - \frac{1}{e} \text{ grad } \zeta, \quad (3.3)$$

$$Q = \pi J + \kappa \text{ grad } T - \frac{1}{e} \zeta J, \quad (3.4)$$

$$\rho = L_1^{-1} \text{ — the electric resistivity,} \quad (3.5)$$

$$\kappa = \frac{L_4 - L_3 L_1^{-1} L_2}{T} \text{ — the thermal conductivity,} \quad (3.6)$$

$$\varphi = \frac{1}{T} \left( \frac{\zeta}{e} + L_2 L_1^{-1} \right) \text{ — the Seebeck coefficient,} \quad (3.7)$$

$$\pi = T\varphi \text{ — the Peltier coefficient.} \quad (3.8)$$

Later on we shall be interested only in longitudinal components of the current density and energy flux density operators, so we shall set  $L_i = L_i^{\mu\nu} = L_i^{xx} = L_i$  ( $i = 1, \dots, 4$ ). The kinetic coefficients  $L_i$  can be expressed by correlators of the operators  $J$  and  $Q$  and when there is no magnetic field we have

$$L_1 = \beta \int_0^\infty dt e^{-nt} \langle J_x J_x(t) \rangle, \quad L_2 = \beta \int_0^\infty dt e^{-nt} \langle J_x(t) Q_x \rangle, \quad (3.9)$$

$$L_3 = L_2, \quad L_4 = \beta \int_0^\infty dt e^{-nt} \langle Q_x(t) Q_x \rangle, \quad (3.10)$$

$$J_x(t) = e^{i\tilde{H}t/\hbar} J_x e^{-i\tilde{H}t/\hbar}, \quad \beta = \frac{1}{kT},$$

$$Q_x = -\frac{1}{2e} (J_x H_e + H_e J_x). \quad (3.11)$$

Within the lowest order approximation with respect to  $H_1$  the following expressions determining the Seebeck coefficient are found

$$\varphi(\sigma) = \frac{1}{eT} (\zeta - \varepsilon_\sigma), \quad (3.12)$$

$$\varepsilon_\sigma = \varepsilon - \varepsilon_p - \varepsilon_m(\sigma), \quad (3.13)$$

$\varepsilon_m(\sigma)$  is determined by the last term in (2.13) and can be written in the form

$$\varepsilon_m(\sigma) \cong A \frac{S(S+1) + \langle (S^z)^2 \rangle}{1 - 4\sigma S - 4\sigma [\langle (S^z + S)^2 \rangle]^{1/2}}. \quad (3.14)$$

For  $A > 0$  the energy level  $\varepsilon_m(-1/2)$  lies below the level  $\varepsilon_m(1/2)$  and for  $A < 0$  the situation is opposite.

Eq. (3.12) implies that thermoelectric power is a function of  $\sigma$ , i. e.  $\varphi = \varphi(\sigma)$ . Hence, taking into account (3.13), we rewrite (3.12) as follows

$$\varphi(\uparrow) = -\frac{1}{eT} [\varepsilon - \zeta - \varepsilon_p - \varepsilon_m(\uparrow)], \quad (3.15)$$

$$\varphi(\downarrow) = -\frac{1}{eT} [\varepsilon - \zeta - \varepsilon_p - \varepsilon_m(\downarrow)]. \quad (3.16)$$

Thus, in a general case we deal with the transport in the "two-band" system. When both sub-bands can contribute simultaneously to the thermoelectric power then the thermoelectric power is given by

$$\varphi = \frac{\Sigma(\uparrow)\varphi(\uparrow) + \Sigma(\downarrow)\varphi(\downarrow)}{\Sigma(\uparrow) + \Sigma(\downarrow)}, \quad (3.17)$$

where  $\Sigma(\sigma)$  is the electric conductivity in the sub-band  $\sigma$ . Let us denote by

$$\Delta(T) = \varepsilon_m(\downarrow) - \varepsilon_m(\uparrow) \quad (3.18)$$

an energy gap formed as a result of the splitting of the polaron levels by the exchange interactions. Then using (3.18) we rewrite Eq. (3.15) in the form

$$\varphi(\uparrow) = -\frac{1}{eT} [\varepsilon - \zeta - \varepsilon_p - \varepsilon_m(\downarrow) + \Delta(T)]. \quad (3.19)$$

A gap width  $\Delta(T)$  will be found from (3.14), generally we can write

$$\Delta(T) = AF(T). \quad (3.20)$$

The explicit form of the  $F(T)$  can be found by calculating the  $\varepsilon_m(\sigma)$  in an appropriate temperature range from both below, and above the Curie temperature  $T_c$ . With  $2|\langle S^z \rangle| > 1$  we get

$$F(T) \cong -4[S(S+1) + \langle (S^z)^2 \rangle] \frac{S + \sqrt{(S^z + S)^2}}{1 - 4(S + \sqrt{\langle (S^z + S)^2 \rangle})^2}, \quad (3.21)$$

hence for  $S \gg 1$

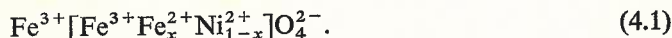
$$F(T = 0) = 2S + 1. \quad (3.22)$$

It means that the exchange interactions in the system cause the splitting of the energy levels into sub-levels separated by  $(2S+1)|A|$  from each other (when  $T = 0K$  and  $S \gg 1$ ). If the widths of these sub-levels are less than the created energy gap we have the two-sub-level system.

Much experimental data can be understood provided that the exchange splitting  $\Delta(T)$  of the energy levels is still finite for  $T \geq T_C$ . At  $T_C$  the long-range magnetic order vanishes, but the short-range order remains and might eventually be responsible for a non-vanishing exchange gap  $\Delta(T)$  at  $T \geq T_C$ . Studying the behaviour of the  $\Delta(T)$  for  $T \geq T_C$  is a complicated and till now unsolved problem.

#### 4. Thermoelectric power in spinel ferrite

The theory presented in §3 will be applied to interpret the experimental data [2, 3, 8] for nickel ferrite (see Fig. 1). The nickel ferrite, ( $T_C = 858$  K) has a crystalline structure of the inversed spinel and can be described by



It is an intrinsic ferrimagnetic semiconductor with a forbidden optical gap about 1.1 eV. Transport in this ferrite is determined by a hopping motion of the carriers, taking place among the iron ions in the  $B$  sub-lattice. The whole  $B$  sub-lattice has a ferromagnetic spin arrangement, the spins are localized on the ions forming this sub-lattice. According to the formula (4.1)  $2N$  is the number of the  $B$  sub-lattice ions,  $N$  is the number of the  $\text{Fe}^{3+}$  ions in the  $B$  sub-lattice,  $xN$  is the number of the  $\text{Fe}^{2+}$  ions in the  $B$  sub-lattice,  $(1-x)N$  is a number of the  $\text{Ni}^{2+}$  ions being in the  $B$  sub-lattice, too. A relative concentration of the  $\text{Fe}^{2+}$  ions, in the sub-lattice under consideration, is

$$\frac{xN}{N+xN} = \frac{x}{1+x} = c. \quad (4.2)$$

The electric conductivity of the involved ferrite is of an  $n$  type and hoppings of the carriers may be treated as a process of an iron ion valence change  $\text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^3 + \text{Fe}^{2+}$ . So, the number of carriers (polarons)  $n$  in a region of a complete  $\text{Fe}^{2+}$  ion ionization does not depend on the temperature and is equal to the number of the  $B$  sub-lattice  $\text{Fe}^{2+}$  ions i.e.  $xN$ .

Neglecting the exchange splitting we have, in our ferrite a set composed of  $(1+x)N$  double degenerated levels (for simplicity we assume that these levels are  $s$  type) and  $2(1+x)N$  states which can be occupied by the polarons. Owing to the exchange interactions these levels are split into two sub-sets of levels. Of course these interactions also remove the spin degeneration. One sub-set, for  $A > 0$ , let us call it the upper one, may be occupied by the up spin polarons (the external magnetic field is oriented along the  $Oz$  axis, the spins point to the opposite direction). The lower sub-sets of the levels may be occupied by the down spin carriers. In the case when  $A < 0$  the position of the levels become inverse. These sub-sets form the sub-bands, which can be occupied by the appropriate spin oriented carriers. The number of carriers in the upper and lower sub-bands is

$$n_{\uparrow} = \frac{(1+x)N}{1 + \exp \left[ \frac{\varepsilon - \zeta - \varepsilon_p - \varepsilon_m(\uparrow)}{kT} \right]}, \quad (4.3)$$

and

$$n_{\downarrow} = \frac{(1+x)N}{1 + \exp\left[\frac{\varepsilon - \zeta - \varepsilon_p - \varepsilon_m(\downarrow)}{kT}\right]} \quad (4.4)$$

respectively.

As we have mentioned above we have  $xN$  carriers (as many as the two valent iron ions in the sub-lattice  $B$ ). Thus

$$n_{\uparrow} + n_{\downarrow} = xN. \quad (4.5)$$

Taking into account (3.18) and inserting (4.3) and (4.4) into (4.5) we get

$$\varepsilon - \zeta - \varepsilon_p - \varepsilon_m(\downarrow) = kT \ln \left[ \frac{1+d + \sqrt{(1+d)^2 + 4dx(2+x)}}{2dx} \right], \quad (4.6)$$

where  $d = \exp(\Delta(T)/kT)$ .

Now we insert (4.6) into (4.5) and we write (3.19) in the form

$$\varphi(\uparrow) = -\frac{k}{e} \ln \left[ \frac{1+d + \sqrt{(1+d)^2 + 4dx(2+x)}}{2x} \right], \quad (4.7)$$

$$\varphi(\downarrow) = \frac{k}{e} \ln d + \varphi(\uparrow). \quad (4.8)$$

For  $AF(T)/kT \gg 1$ ,  $d \gg 1$  we find

$$\varphi(\uparrow) = -\frac{AF(T)}{eT} - \frac{k}{e} \ln \frac{1}{x}, \quad (4.9)$$

$$\varphi(\downarrow) = -\frac{k}{e} \ln \frac{1}{x}, \quad (4.10)$$

and for  $AF(T)/kT \ll 1$ ,  $d \simeq 1 + AF(T)/kT \simeq 1$

$$\varphi(\uparrow) = -\frac{k}{e} \ln \frac{1 + \sqrt{1+x(2+x)}}{x} = \varphi(\downarrow). \quad (4.11)$$

The results of paper [2] are described by Eq. (4.7). It means that, in the ferrite under consideration, the transport takes place in the upper sub-band (the up spin polarons are the carriers) and the  $s$ - $d$  exchange integral should have a plus sign.

Knowing the experimental dependence  $\varphi(\uparrow) = \varphi(T, x)$  we can determine the temperature dependence of the energy gap  $\Delta(T) = \Delta(T, x)$  from Eq. (4.7). After simple calculations we get

$$\Delta(T, x) = kT \ln \frac{x e^{\frac{|e|\varphi(T, x)}{k}} - 1}{1 + (2+x) \exp\left[-\frac{|e|\varphi(T, x)}{k}\right]}.$$

From here after having inserted a value of  $\varphi(T, x)$  for  $x = 0.13$  from [2] we get the curve shown in Fig. 1 (curve *a*). In the same figure (curve *b*) the  $\Delta(T)$  dependence according to (3.20) and (3.21) for the range  $T < T_C$ , is shown. The dotted part of the curve *b* has been found within a molecular field approximation to Eq. (3.21), then the condition  $2|\langle S^z \rangle| > 1$  is not however fulfilled, and this part of the curve should be treated with scepticism.

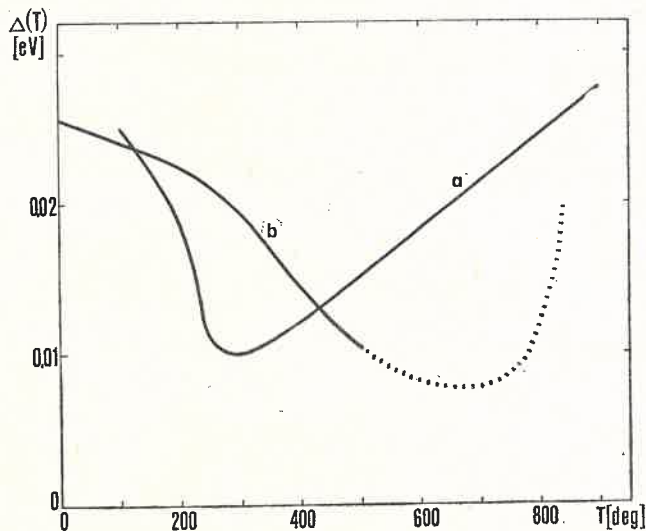


Fig. 1.  $\Delta(T)$  vs  $T$  (details are given in the text)

To make a comparison we recall now the idea and the results of the theory [2]. The authors of [2] assumed the energy levels of the  $\text{Fe}^{2+}$  ions to be split into two sub-bands separated by the energy gap  $E_0$  (in the general number of the levels they took into account the  $\text{Fe}^{3+}$  ion levels from the sub-lattice *B* as well). In the upper sub-band there are  $p(1+x)N$  conducting levels, the number of polarons in them is

$$n_{1p} = \frac{p(1+x)N}{1 + \exp \frac{E_0 - \zeta}{kT}} \quad (4.12)$$

There are also  $(1-p)(1+x)N$  non-conducting levels in the upper sub-band the number of carriers in them is

$$n_{1np} = \frac{(1-p)(1+x)N}{1 + \exp \frac{E_0 - \zeta}{kT}} \quad (4.13)$$

Analogously there are  $p(1+x)N$  conducting levels in the lower<sup>2</sup> sub-band with the number of carriers

$$n_{2p} = n_{1p} \quad (4.14)$$

<sup>2</sup> In the general case  $p$  may be different for each sub-band.



Non-conducting levels in the lower sub-band are  $(1-p)(1+x)N$  with the following number of carriers

$$n_{2np} = n_{1np} \quad (4.15)$$

There are  $xN$  polarons, which can be occupied the levels in both sub-bands. Let us write then

$$n_{1p} + n_{2p} + n_{1np} + n_{2np} = xN. \quad (4.16)$$

The authors of that paper assumed both that the transport takes place only in the upper sub-band i.e.  $n_{2p} = 0$  and the upper band non-conducting levels are not occupied i.e.  $n_{1np} = 0$ . Now (4.16) has the form

$$n_{1p} + n_{2np} = xN. \quad (4.17)$$

Inserting (4.12) and (4.15) into (4.17) we get an equation which determines the chemical potential  $\zeta$ . Solving this equation and rejecting unphysical solutions we find

$$-\zeta = kT \ln \left[ \frac{D}{2B} \left( 1 + \sqrt{1 + \frac{4B}{D^2}} \right) \right], \quad (4.18)$$

where

$$D = p(1+x) - x + [1 - p(1+x)] \exp E_0/kT, \quad B = x \exp (E_0/kT).$$

Inserting (4.18) to the expression below

$$-e\varphi T = E_0 - \zeta, \quad (4.19)$$

we have<sup>3</sup>

$$\varphi = -\frac{E_0}{eT} - \frac{k}{e} \ln \left[ \frac{D}{2B} \left( 1 + \sqrt{1 + \frac{4B}{D^2}} \right) \right], \quad (4.20)$$

$$\varphi = -\frac{E_0}{eT} - \frac{k}{e} \ln \left[ \frac{1 - p(1+x)}{x} \right] \quad \text{for } E_0/kT \gg 1,$$

$$\varphi = -\frac{k}{e} \ln \frac{1}{x} \quad \text{for } E_0/kT \ll 1. \quad (4.21)$$

From a comparison with the experimental results, the authors estimated  $p$  and came to a conclusion that  $p < 0.2$ .

For a comparison with the experimental data of [2, 3],  $\varphi$  given by (4.7) is plotted vs  $10^3/T$  for  $x = 0.13$  (curve 2a),  $x = 0.21$  (curve 3a) and  $x = 0.4$  (curve 6a) in Fig. 2.

<sup>3</sup> There are some misprints in equation (6) and the previous one in paper [2].

Because of the weak temperature dependence of  $F(T)$  we set  $F(T) = \text{const}$ . Hence the sign and the magnitude of the  $s$ - $d$  exchange integral were determined. The estimated value is of the order of  $10^{-2}$  eV.

It follows from Fig. 2 that the qualitative agreement with the experiment is better in the case of the theory constructed on the basis of the hopping mechanism of the

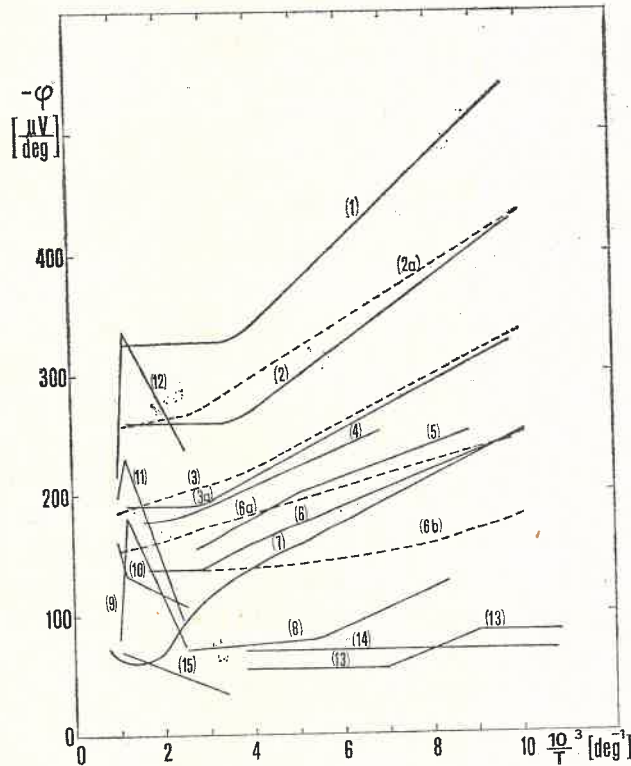


Fig. 2. The Seebeck coefficient vs  $10^3/T$ . Curves 1 for  $x = 0.076$ , 2 for  $x = 0.13$ , 3 for  $x = 0.21$  are taken from [2]; curves 4 for  $x = 0.2$  and 6 for  $x = 0.4$  from [3]; curve 5 for  $\text{NiFe}_2\text{O}_4$  from [5]; curve 7 for  $\text{Li}_{0.2}\text{Ni}_{0.8}\text{O}$  from [6]; curve 8 for  $\text{Fe}_3\text{O}_4$  from [7]; curves 9—12 for  $\text{NiFe}_2\text{O}_4$  from [8] for various sintering times of the samples (9 — 5h, 10 — a single crystal, 11 — 0.5 h, 12 — 2h). Theoretical curves 2a, 3a, 6a are plotted according to the Eq. (4.7) for appropriate values of  $x$ . Curve 6a is plotted according to the theory given in [3]. Curves 13 and 14 illustrate the temperature dependence of  $\varphi(T)$  for  $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$  taken from [9]; curve 13 for  $x = 0.2$  and curve 14 for  $x = 0.4$ . Curve 15 for the magnetite after [10]

transport than for that based on the band mechanism of the transport (cf. the theoretical curve 6b in Fig. 2 of [3]).

Poor reproducibility of the experimental data of various authors should be emphasized. In Fig. 2 the results of Constantin [9] are also shown. Curve 13 was obtained for  $x = 0.21$  (to be compared with curve 13) and curve 14, for  $x = 0.4$ , differs considerably from curve 16 of paper [3].

It turns out also that there is a considerable dependence of  $\varphi(T)$  on the kind of applied contacts in the course of an experiment. That dependence is illustrated by the curves 4-7 in Fig. 3 (see Ref. [13]). In Fig. 3 there are also curves illustrating the dependence of  $\varphi(T)$  for other ferrites. Details are given in the legend of Fig. 3.

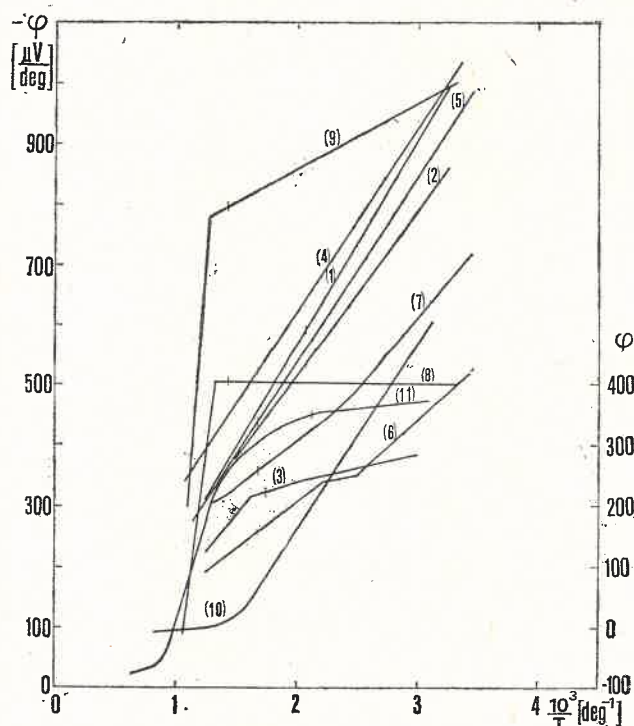


Fig. 3.  $\varphi$  vs  $10^3/T$  for different ferrites after different authors. Curves 1 and 2 for single crystals  $Mn_{1.45}Fe_{1.55}O_4$ ; curve 1 for slowly cooled and curve 2 for a quenched sample [11] (dash indicates  $10^3/T_c$ ). Curve 3 is plotted for a single crystal  $MnFe_2O_4$  [12]. Curves 4 - 7 illustrate the Seebeck coefficient dependence on the kind of the contacts which were used in the course of studying the same sample  $Mn_xFe_{3-x}O_4$  contacts (4 - finely ground surface; 5 - etched in KCl; 6 - contacts from silver paste, annealed at 450 K; 7 - contacts from In-Ga alloy) [13]. Curves 8 and 9 show the Seebeck coefficient dependence on  $T$  measured in different directions with respect to the axis  $c$  of the single crystal  $PbFe_{12}O_{19}$  (8 -  $\perp c$ ; 9 -  $\parallel c$ ) [14]. Curve 10 is plotted for  $CoFe_2O_4$  and curve 11 - for  $Co_{1.01}Fe_{1.99}O_4$  after [15] (a right hand side axis)

### 5. Conclusions

Results of the experimental data of the thermoelectric power in the ferrites under consideration are best described by the hopping mechanism with a polaron as an electric charge carrier. An important role is played by the exchange interaction which causes the energy levels to split. An energy gap created by this interaction does not vanish at  $T_c$  and remains finite even when  $T > T_c$ .

Insufficient reproducibility of the known up to now experimental data (see Figs 2 and 3) does not allow one to find the precise temperature dependence of the exchange gap

in the whole temperature range. It would be of special importance to measure the thermoelectric power in a paramagnetic region. A comparison of the experimental data for the thermoelectric power with the theory makes it possible to estimate the  $s$ - $d$  exchange interaction integral. For the discussed ferrites this estimate gives a surprisingly small quantity of the order of  $10^{-2}$  eV.

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