SEMICONDUCTOR PROPERTIES OF $Ni_{1-x}Zn_xFe_2O_4$ FERRIMAGNETICS FOR $0 \leqslant x \leqslant 1$*

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(Received October 18, 1968)

$Ni_{1-x}Zn_xFe_2O_4$ ferrimagnetics with $0 \leqslant x \leqslant 1$ are semiconductors in which $3d$ electrons are carriers of electric charge as well as of spin magnetic moment, and participate in exchange interactions leading to ferrimagnetic type of ordering.

The effect of magnetic structure of NiZn ferrites on the generation energy and mobility of the electric current was studied. To this aim, the temperature dependence of electric conductivity σ and Seebeck effect θ in the temperature range from 500°K to 1000°K was determined. The results are interpreted on the basis of the crystal field theory and assuming the Verwey model for electric conductivity in $3d$ oxides.

Magnetic ordering is found to lower the generation energy of carriers, and their mobility is then independent of their density.

Introduction

With regard to magnetic structure, ferrites are ferrimagnetics, whereas with regard to temperature-dependence of their electric conductivity they are semiconductors, both properties being determined by the same $3d$ electrons of iron ions. Hence, interaction between the electric current carriers and magnetic structure in ferrites presents a high degree of interest.

Various authors have shown experimentally that ferrites in general exhibit an anomaly of the electric conductivity σ at the Curie temperature T_c[1—5]. This anomaly has also been dealt with theoretically [6–8]. Anomalies of the Seebeck effect θ at the Curie point T_c have also been observed [9–12]. On the other hand Jonker [12], who investigated cobalt ferrite, does not mention anomalous behaviour of θ at T_c. Samokhvalov and Men' [14] derived an interesting theoretical result for the value of the energy gap between the ground state and excited state for the Fe^{2+} ion at the octahedral site of spinel. Considering spin-orbit inter-

* Part of the present results has been reported at the Poznań International Ferromagnetic Colloquium of 1964.

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action only, they obtained an energy gap of about 0.01 eV dependent on the composition and structure of neighbourhood of the Fe^{2+} ion.

The present paper gives results on the effect of magnetic ordering in $Ni_{1-x}Zn_xFe_2O_4$ ferrites with $0 \leqslant x \leqslant 1$ on the energy of generation of the electric current carriers and on their mobility. From the temperature-dependence of σ and θ between 500° and 1000°K, and basing on the theory of thermoelectric phenomena as proposed by Tsuji [15] for semiconductors of the Verwey type, the generation energy of carriers is calculated, and their mobility is determined from the shape of σ (T).

Experimental

1. Preparation of specimens

Polycrystalline specimens were prepared by sintering pure oxides NiO, ZnO and Fe_2O_3 in a sylite furnace in air. The oxide mixture was ground during 12 hrs in steel ball mills. Prefiring the powder mixtures was carried out at 1330°K in air during 1 hour. After re-grinding, disks were shaped by compressing at 500 at. The disks were sintered in air at 1470°K in three portions, respectively during 30 min., 2 hrs and 5 hrs. Cooling in the furnace down to room temperature lasted about 10 hrs.

Electrodes were deposited by heating silver paste at 900°K on the surface, whence by surface polishing layers of thickness more than 100 times the grain size were obtained.

The specimens had the shape of parallelepipedes of dimensions about $5 \times 3 \times 1$ mm.

2. Structure of the specimens

The density from Archimedes law amounted to about 93 per cent of X-ray density and did not depend on the time of sintering, proving that the oxides had totally gone over into spinel. X-ray investigation revealed spinel structure in all specimens, and the lattice constant fulfilled the Vegard rule concerning linear dependence between the lattice constant and the concentration of one of the components.

In specimens heated to 1300°K X-ray investigation revealed neither a new phase, superstructure, nor a change of symmetry.

Chemical analysis yielded a Ni content by about 1 per cent higher than the stoichiometrical one. The amount of Fe^{2+} ions in the specimens ranged from several tenths of one per cent for $0.4 \leqslant x \leqslant 0.7$ down to less than 0.05 per cent — the limit of sensitivity of the method.

Magnetisation σ_n at saturation as determined in a field of 8 kOe by the ballistic method, as well as the Curie point T_c, were in accordance with the literature data.

3. Methods of measuring θ and σ

Measurements of the electric conductivity σ and Seebeck's effect θ *versus* the temperature T were performed simultaneously for the same temperature. $\sigma(T)$ was determined by means of a Wheatstone bridge, whereas $\theta(T)$ by measuring the thermoelectromotive force with a compensator circuit. The temperature was determined by chromonickeline-constantan thermocouples and a compensator to within $\pm$ 2 deg and the difference in tempearature, which

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amounted to about 10 deg to within ± 0.05 deg. Deposition of new silver paste electrodes on surfaces from which earlier electrodes had been removed by polishing entailed a change in θ by no more than several hundredths mV/deg. and did not affect the shape of $\theta(T)$, while remained altogether unaffected.

4. Results of measurements

The results obtained for $\sigma(T)$ and $\theta(T)$ are exemplified for several specimens in Figs 1–4. The graphs served for calculating the activation energy of electric conductivity q as well as the generation energy of current carriers Δ for various compositions of the specimens and various temperatures.

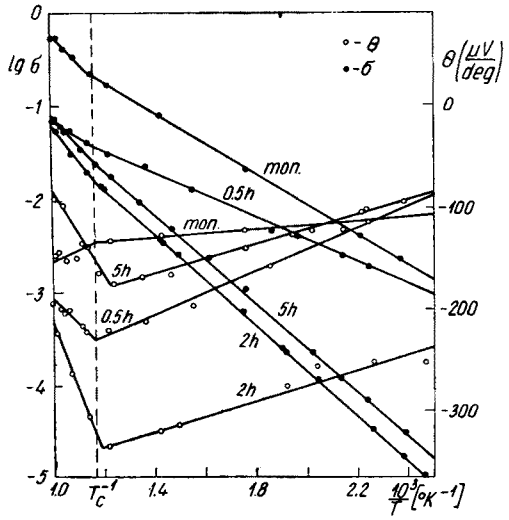

Fig. 1. Temperature dependence of Seebeck coefficient θ and electric conductivity σ for $NiFe_2O_4$ ferrite single crystal, and for polycrystalline specimens sintered at 1470°K. The sintering time is marked as a parameter

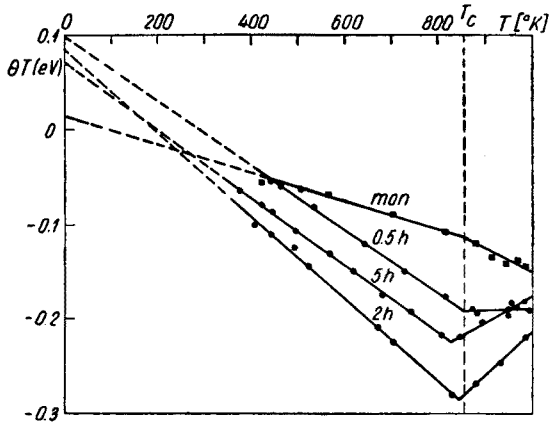

Fig. 2. Temperature-dependence of θT (Peltier coefficient) for $NiFe_2O_4$ ferrite single crystal, and for polycrystalline specimens sintered at 1470°K. The sintering time is marked as a parameter

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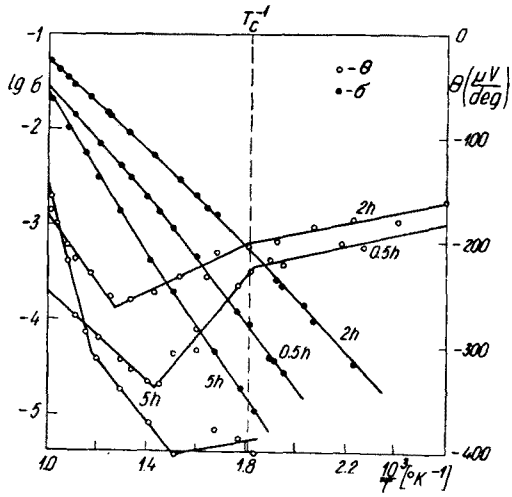

Fig. 3. Temperature-dependence of Seebeck coefficient θ and electric conductivity σ for $Ni_{0,5}Zn_{0,5}Fe_2O_4$ ferrite specimens sintered at 1470°K during 30 min, 2 hrs and 5 hrs, respectively

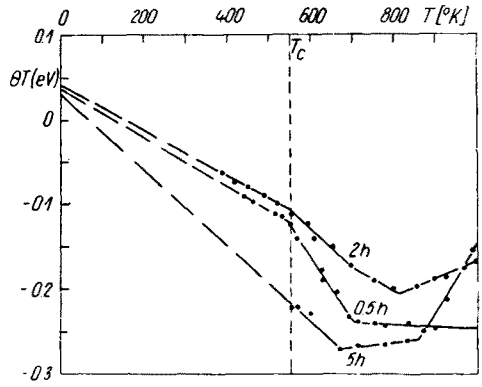

Fig. 4. Temperature-dependence of θT (Peltier coefficient) for $Ni_{0,5}Zn_{0,5}Fe_2O_4$ ferrite sintered at 1470°K during 30 min, 2 hrs, and 5 hrs, respectively

Interpretation of the results

Conductivity in the ferrites was assumed to be of "hopping process" type. For this type of semiconductors, we have by the Tsuji's theory [15].

$$\theta T = \frac{\sigma_d (Q_d + \mu - E_1) - \sigma_e (Q_e + E_2 - \mu)}{\sigma_d + \sigma_e}$$

where θ is the Seebeck coefficient, σ_d and σ_e the hole and electron conductivity, respectively, Q_d and Q_e quantities proportional to the transition probability of a hole and an electron from one ion to another per unit time, μ the chemical potential, and E_1, E_2 the excited state energies respectively for an Fe^{2+} and an Fe^{4-} ion.

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If carriers of one sign (*e. g.* electrons) predominate, one has

$$\theta T = -(Q_e + E_2 - \mu)$$

The generation energy of carriers, $\Delta = E_2 - \mu$, was determined from the dependence of θT on T. The Δ values thus obtained for various compositions are shown in Fig. 5 for magnetic ordering, and in Fig. 6 when such an ordering had been destroyed thermally.

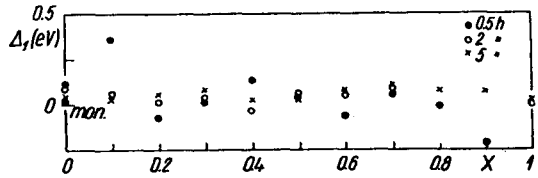

Fig. 5. Generation energy Δ_1 for electric current carriers as a function of the composition of specimens sintered at 1470°K during 30 min, 2 hrs and 5 hrs, respectively, in the presence of magnetic ordering

The values of Δ_1 in the presence of magnetic ordering are almost independent of the composition and amount to approximately 0.03 eV for most specimens, a value close to that of Men' and Samokhvalov [14].

The situation is, however, entirely different at higher temperatures, when magnetic ordering has been abolished. The generation energy Δ_2 is now larger than Δ_1 and exhibits an involved dependence on the composition. In most specimens Δ_2 decreases linearly from

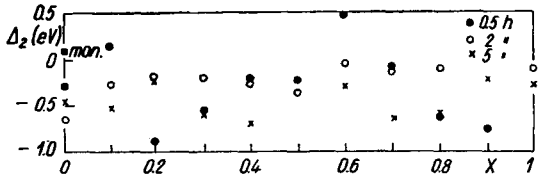

Fig. 6. Generation energy Δ_2 of electric current carriers as a function of the composition of specimens sintered at 1470°K during 30 min, 2 hrs and 5 hrs, respectively, in the absence of magnetic ordering

0.3 eV to 0.1 eV as the number of iron ions in octahedral spinel sites increases. On the other hand, magnetic ordering is clearly seen to cause a considerable decrease in generation energy of the current carrier.

The physical meaning of the generation energies Δ_1 and Δ_2 can be defined by considering a "hopping process" within the framework of ligand-field theory. Verwey suggested that the "hopping process" in ferrites consisted in electron jumps between Fe^{2+} and Fe^{3+} or between Fe^{3+} and Fe^{4+} ions statistically situated at octahedral spinel sites. From ligand--field theory [16], d^5-ions (and Fe^{3+} is precisely of this type) are strongly recalcitrant with regard both to addition and to detachment of d-electrons. When a fifth electron is added to an ion with d^4-configuration, its spin in accordance with Hund's rule will assume a position parallel to those of the four electrons already present in the ion, and will thus be strongly

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stabilized by exchange interaction. However, a sixth electron will have its spin antiparallel to the five others and will be more weakly bound to the d^5-ion. Hence carrier generation energy is the amount of energy necessary for detaching a sixth electron from a Fe^{2+}-ion and attaching it as sixth d-electron to a Fe^{3+}-ion, or for detaching a fifth d-electron from a Fe^{3+}-ion and bonding it as fifth electron to a Fe^{4+}-ion.

Moreover, one can give the diffusion length of an electron between Fe ions basing on Wollan's model [17] of exchange interactions in spinel in the approach of the ligand-field theory.

When a metal ion of the transition group is carried over into octahedral surroundings, the d-orbitals split into t_{2g}-orbitals of lower and e_g-orbitals of higher energy. The t_{2g}-orbitals have their electron densities concentrated between the ligands, whereas those of the e_g-orbitals are concentrated near the ligands. The electron distribution over orbitals in the ions in a weak ligand field at the octahedral sites (this is just the case for spinels) is the following [16]:

TABLE 1

Ion	Number of d-electrons	t_{2g}-level	e_g-level
Fe^{2+}	6	↑ ↓ ↑ ↑	↑ ↑
Fe^{3+}	5	↑ ↑ ↑	↑ ↑

In our case, we are concerned only with B-B interaction *i. e.* with interaction of ions at octahedral sites, since only such ions play a part in electric conductivity. For this kind of interaction, one can expect simple overlapping of t_{2g}-orbital wave functions [17] implying presence of electron exchange between the ions distributed over the octahedral sites. Now, this type of interaction leads to antiferromagnetic ordering in accordance with Néel's theory [18] and as confirmed by the properties of ferrites having the structure of normal $ZnFe_2O_4$ spinel [19]. B-B interaction is weak, and is disrupted in inversed spinels by strong A-B antiferromagnetic interaction. The latter occurs between electrons from e_g-orbitals of B ions and electrons from t_{2g}-orbitals of A ions through the intermediary of p-levels of O^{2-}-ions. Whereas there are two kinds of orbitals (t_{2g} and e_g) in ions at B-type sites, in the ferrites t_{2g}-orbitals can correspond only to those levels in which electric current carriers originate (this statement will be demonstrated later on). The carriers in passing from one ion to another, jump only from one of these levels to another owing to interaction with phonons. Weak overlapping of the t_{2g}-orbital wave functions is maybe an indication that a "quasi" conduction band appears. This provides a first possible diffusion length of electrons between Fe-ions.

Let us consider yet another possibility of electron exchange between Fe^{2+} and Fe^{3+}-ions at octahedral spinel sites. Thermal excitation of an electron from a t_{2g}-level to an e_g-level can occur in an Fe^{2+}-ion. From the e_g-level, by way of the p-level of an O^{2-}-ion, the electron passes to an e_g-level of an Fe^{3+}-ion, which then becomes an Fe^{2+}-ion with excited e_g-level. The electron now goes over into the ground state t_{2g} or remains on the e_g-level for a time interval longer than the time of transition from one ion to another, and then jumps over

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to an Fe^{3+}-ion. In reality, owing to hybridization of the $2s$ and $2p$ wave functions or excitation of $2p$ electrons to the $3d$-level, there can be weak overlapping of orbitals of the B-ion and those of the anion. As shown by Zener [20], this leads to an exchange interaction different from superexchange. If e_g Fe^{2+} and Fe^{3+}-ions are present in B-sites, an electron passes from an Fe^{2+}-ion to an O^{2-}-ion and simultaneously an electron goes over from O^{2-}-ion to an Fe^{3+}-ion. Such motion of electrons causes interaction of the ferromagnetic kind between the ions (in the present case, between the iron ions).

From this approach, an increase in the number of Fe^{2+}-ions will result in higher electric conductivity. However, the temperature-dependence of σ derived by Zener [20] for this model and taking into account the preceding exchange interaction was of the $\sigma \sim \frac{1}{T}$ type, whereas experimentally it is found to be $\ln \sigma \sim \frac{1}{T}$. Thus, Zener's model [20], though acceptable by intuition, proces to yield a result not in agreement with experiment. Hence, the possibility of electron jumps from Fe^{2+}-to Fe^{3+}-ions by way of O^{2-}-ions has to be rejected.

In the interpretation of Seebeck's effect in $3d$ oxides, one assumes that $3d$ carriers do not transport kinetic energy because they spend most of the time captured in lattice nodes. There is thus no effect of phonon drag, and the Seebeck effect is due solely to the gap between the carrier level and the Fermi level [21]. In this case, in spinels as a result of magnetic ordering the gap changes by an amount much in excess of the exchange energy kT_c. Things are similar in V_2O_3 [21] on transition through T_N.

We now proceed to an analysis on the electric conductivity, whose temperature-dependence is exemplified for several specimens in Figs 1 and 3. For our conclusions, we shall recur to Heikes and Ure's formula [22] for semiconductors of the "hopping process" type:

$$\sigma = \text{const}\, n(N-n)\, T^{-1}\, \tau_0^{-1} \exp\left(-\frac{q}{kT}\right)$$

with the notation: $(N\text{-}n)$ density of all sites to which an electron can go jumpwise, n density of carriers, τ_0^{-1} *a priori* probability of a jump at infinite temperature, q activation energy of electric conduction process σ.

Fig. 7 gives $\sigma_\infty = \text{const}\, n(N\text{-}n)\, T^{-1}\, \tau_0^{-1}$ as a function of the composition. Aproximately, σ_∞ varies linearly with the composition of the specimens in presence therein of magnetic ordering. However, above T_c, the graph of σ_∞ has a marked minimum for specimens with highest content of Fe^{2+}-ions, as proved by chemical analysis. Such a shape of the σ_∞-curve points to a decrease in τ_0^{-1} with growing amounts of Fe^{2+}-ions.

From these qualitative considerations, a higher Fe^{2+}-ion concentration involves less frequent electron jumps. For magnetic ordering, variations in the concentration of Fe^{2+}-ions and thus of the carriers do not affect the mobility of the latter so strongly.

Finally, we have to define what we mean by magnetic ordering. By this, we mean local exchange interaction with nearest neighbours, interaction that does not necessarily lead to magnetic ordering in large regions of the specimen or, still less, in the whole of it. Thus *e. g.* in $ZnFe_2O_4$ ferrite, which is paramagnetic at the temperatures investigated, a change in carrier generation energy was observed to occur at temperatures near T_c of magnetite.

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This latter fact induces one to consider an Fe^{2+}-ion together with its nearest neighbourhood in $ZnFe_2O_4$ as being a magnetite "cluster", wherein exchange interactions between Fe^{2+} and Fe^{3+} undergo thermal destruction only at temperatures that lie close to T_c for magnetite.

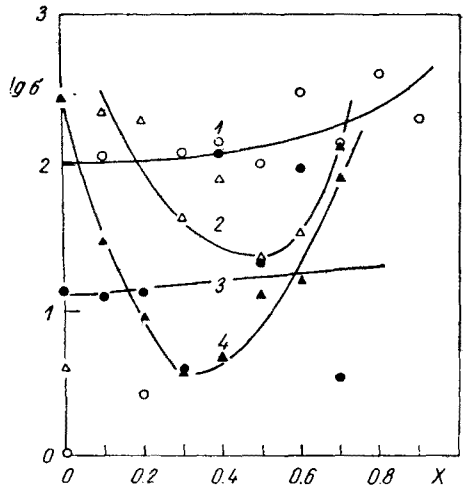

Fig. 7. Coefficient σ_∞ as a function of the composition of $Ni_{1-x}Zn_xFe_2O_4$ specimens sintered at 1470°K during 30 min, 2 hrs and 5 hrs, respectively. Curves *1* and *2* are at magnetic ordering, and curves *3* and *4* in its absence

Ishikawa [23], when studying magnetic properties of NiZn ferrites, found that they presented "clusters". The presence of "clusters" in our ferrites, which have a high Zn content, can be moreover, due to the existence locally of inversed spinel regions owing to conditions of preparation.

The author wishes to thank Professor Dr S. Szczeniowski for his helpful remarks throughout this investigation.

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