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EFFECT OF MAGNETIC ORDER ON THE CONDUCTIVITY IN Co–Zn FERRITES

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A series of samples in the system $Co_{1-x}Zn_xFe_2O_4$ (x=0.3, 0.4, 0.6, 0.8 and 1) were prepared by the usual ceramic technique. The D. C. electrical resistivity and thermoelectric power were measured in the temperature range from room temperature up to about 600 K. Transition from the ferrimagnetic region to the paramagnetic region is accompained by an increase in the activation energy by an amount ΔE, which varies in the range 0.052–0.090 eV. The large values of ΔE obtained may be due to the fairly strong B–B exchange interaction in Co–Zn ferrites.

Ferrites are semiconductors; depending on the chemical composition, their resistivity can vary between about 10^{-2} ohm·cm and higher than 10^{11} ohm·cm. The resistivity for ferrites decreases with increase of temperature according to the equation:

$$\varrho = \varrho_\infty e^{E/KT}$$

where E is the activation energy needed to release an electron hopping from an ion to the neighbouring ion, thereby giving rise to electrical conductivity [1].

The transition from the ordered ferrimagnetic state to the paramagnetic state in ferrites is accompained by changes in physical properties. The activation energy for electrical conductivity has been found to be smaller in the ferrimagnetic state than in the paramagnetic state [2–4]. In another work [5], no change in activation energy was detected at the transition temperature.

Thermo e.m.f. measurements have been made for a series of ferrites $Co_{1-x}Fe_{2+x}O_4$ [6]. These revealed two regions of conductivity. The first region was of p-type, containing Co^{2+} and Co^{3+}; the other region was of n-type, containing Fe^{2+} and Fe^{3+} ions. Nickel ferrite was studied [7] and the electrical conductivity of $NiFe_2O_4$ with a small Co substitution confirmed the idea of cobalt existing in the ferrite in two valence states.

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The aim of the present work is to study the behaviour of the D.C. conductivity and thermoelectric power α for Co–Zn ferrites during the transition through the Curie temperature.

Experimental

A series of samples in the system $Co_{1-x}Zn_xFe_2O_4$ (x = 0.3, 0.4, 0.6, 0.8 and 1) were prepared by the usual ceramic technique. The samples are sintered at 1200° for 2 h and slowly cooled in the furnace to room temperature. X-ray analysis showed that they are cubic spinel (single phase).

The temperature-dependences of the electrical resistivity ϱ and the thermoelectric power α were measured. The samples were polished, smoothly ground and rubbed with silver paste as a contact material. NiCrNi thermocouples were used to measure the temperature. The sign of the thermovoltage was determined from the polarity of the cold end of the specimen as the charge carriers diffuse from the hot to the cold part. The thermovoltage divided by the temperature difference gives the thermoelectric power. Details of the apparatus used are given elsewhere [5].

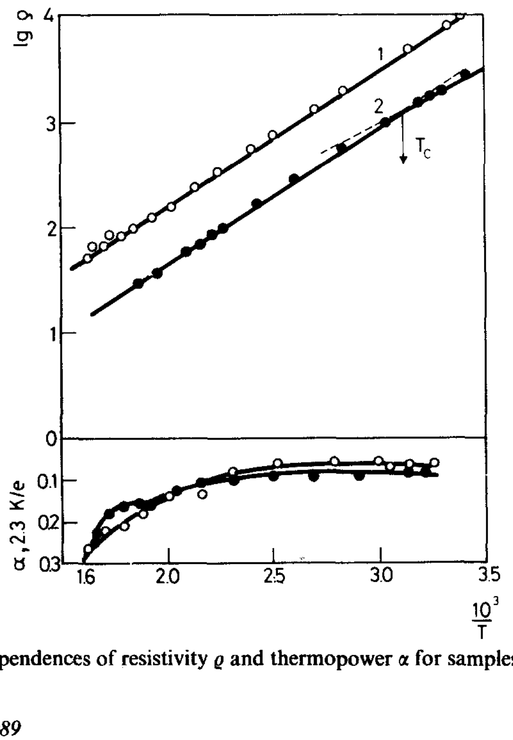

Fig. 1 Temperature-dependences of resistivity ϱ and thermopower α for samples 1 and 2 (see Table 1)

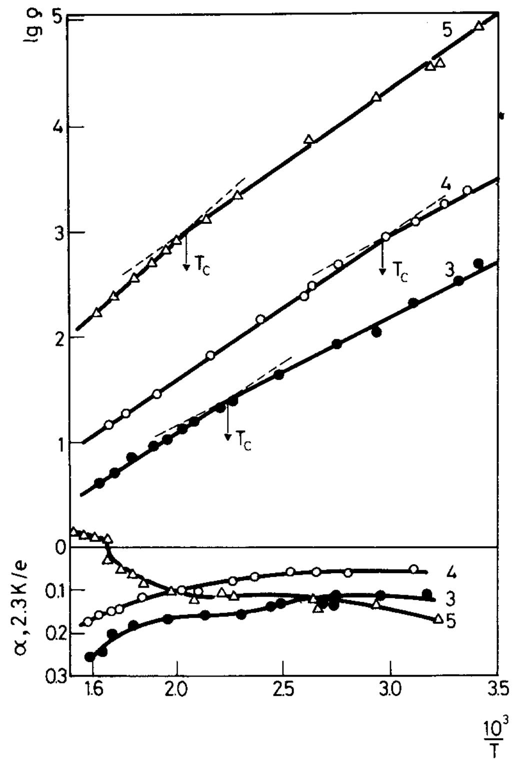

Fig. 2 Temperature-dependences of resistivity ϱ and thermopower α for samples 3, 4 and 5 (see Table 1)

Results

Figures 1 and 2 give the temperature-dependence of the DC resistivity ϱ and the thermoelectric power α for all samples. The activation energy increases after the Curie point is passed. The thermoelectric power expressed in units of 2.3 K/e = 198 μV/deg; it depends on the temperature in the paramagnetic region.

Table 1 gives the values of the activation energy for all samples in the paramagnetic region, E_p (disordered state), and in the ferrimagnetic region E_f (ordered state), the change in activation energy, ΔE and the exchange energy, $E_{ex} = KT_c$, where K is the Boltzmann constant and T_c is the Curie temperature.

Table 1 Comparison between the changes in activation energy, ΔE, for conductivity during transition to the paramagnetic state and the values of the exchange energy, E_i, for some compositions in the system $CoZnFe_2O_4$

Sample no.	Molecular formula	E_f, eV	E_p, eV	ΔE, eV	T_c, K	$E_i = KT_c$, eV
1	$ZnFe_2O_4$	0.246	0.246	0	—	—
2	$Co_{0.2}Zn_{0.8}Fe_2O_4$	0.210	0.262	0.052	317.5	0.027
3	$Co_{0.4}Zn_{0.6}Fe_2O_4$	0.211	0.270	0.059	335.6	0.029
4	$Co_{0.6}Zn_{0.4}Fe_2O_4$	0.204	0.265	0.061	446.4	0.038
5	$Co_{0.7}Zn_{0.3}Fe_2O_4$	0.265	0.355	0.090	487.8	0.042

Discussion and conclusions

In the cubic system of ferrimagnetic spinels, there are two sublattices: tetrahedral A and octahedral B sublattices [8]. The magnetic order is mainly due to superexchange interaction mechanism occurring between the metal ions in the A and B sublattices. There are three types of interactions: A–A, A–B and B–B interactions. Non-magnetic zinc ions occupy positions in the A sublattice, and this causes a decrease in the A–A and A–B interaction forces. Thus, the B–B exchange interactions increase with increasing Zn content.

Mixed Co–Zn ferrites [9] have the formula $Zn_x^{2+}Fe_{1-x}^{3+}(Co_{1-x}^{2+}Fe_{1-x}^{3+})O_4$. During sintering, some of the Fe^{3+} is transformed to Fe_e^{2+}, so electronic conductivity occurs due to exchange of electrons between Fe^{3+} ions and Fe^{2+} ions. The existence of a strong B–B exchange interaction between ions at the B sites of such ferrites will greatly affect the activation energy required for the transfer of an electron between Fe^{2+} and Fe^{3+}. In the present work the results showed a considerable decrease in the activation energy for conduction in the magnetically ordered phase, E_f, and consequently the transition temperature T_c shifts to lower values due to increasing Zn content. Our *DC* resistivity measurements and the values of the activation energies confirm the results published in previous works [10–12]. A similar decrease in the transition temperature due to the Zn content was reported [4] in the case of Ni–Zn ferrites.

The thermoelectric power α for our Co–Zn samples is negative, indicating that electrons are the majority of the carriers at room temperature. It increases in magnitude with temperature in the paramagnetic region. This might be due to activated electron hopping between Fe^{2+} and Fe^{3+}.

Only in the case of $Co_{0.7}Zn_{0.3}Fe_2O_4$ did the thermopower become positive at about 595 K. Thus, the majority of the carriers are holes after this temperature. These results indicate the existence of Co^{2+} in CoZn ferrites, which is in agreement with previous results [6, 7].

Conclusions

1. The transition temperature T_c shifts to lower values with increasing Zn content.

2. The activation energy for conduction in the disordered state decreases with increasing Zn content.

3. Cobalt in Co–Zn ferrites exists in two valence states.

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Zusammenfassung — Mittels üblicher Keramiktechniken wurden Proben des Systemes $Co_{1-x}Zn_xFe_2O_4$ unterschiedlicher Zusammensetzung (x = 0,3, 0,4, 0,6, 0,8, 1,0) dargestellt. Im Temperaturbereich Raumtemperatur-600 K wurde der elektrische Widerstand gegenüber Gleichstrom sowie die Thermospannung dieser Proben ermittelt. Der Übergang von der ferrimagnetischen zur paramagnetischen Region wird von einem Anwachsen der Aktivierungsenergie um den Betrag ΔE = 0,052–0,090 eV begleitet. Den so erhaltenen grossen ΔE-Werten liegen wahrscheinlich die ziemlich starken B–B Austausch Wechselwirkungen in Co–Zn Ferriten zu Grunde.

Резюме — Получен ряд образцов состава $Co_{1-x}Zn_xFe_2O_4$ с x = 0,3; 0,4; 0,6; 0,8 и 1, для которых электрическое удельное сопротивление при постоянном токе и термоэлектрическая сила были измерены в интервале температур от комнатной до 600 K. Переход из ферримагнитной области в парамагнитную сопровождался некоторым увеличением энергии активации ΔE, изменяющимся в интервале 0,052-0,090 эВ. Такие большие значения ΔE могут быть обусловлены сильным B–B обменным взаимодействием в кобальт-цинковых ферритах.