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## TRANSPORT PHENOMENA IN THE MAGNETICALLY MODULATED SPINELS: $Zn_{1-x}Cu_xCr_2Se_4$ (WHERE $0.0 \leq x \leq 1.0$ )

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**Abstract.** – The spinels under study are p-type semiconductors showing a change of the conductivity character from the conductive into metallic one at  $x \sim 0.3$ . An increase of the electrical conductivity with the copper concentration in a sample is linked both with the increase of the hole mobility and the hole concentration. For  $x \geq 0.05$  partial degeneracy of the semiconductor state is observed.

### 1. Introduction

The spinels of the series  $Zn_{1-x}Cu_xCr_2Se_4$  have been studied since many years because of their extremely interesting magnetic and electrical properties [1-5]. The magnetic phase transitions were observed in these spinels from an antiferromagnetic spiral structure for  $x = 0$  through a conical structure for  $0.05 \leq x \leq 0.7$  to a ferromagnetic structure for  $x \geq 0.8$  [3]. The explanation of these properties was based on the assumption of the mixed valence of chromium ( $Cr^{3+}$ ,  $Cr^{4+}$ ) with the concentration of  $Cr^{4+}$  equal to  $x$  (i.e. to the copper concentration) [1, 3]. The aim of this paper is the presentation of the experimental results concerning the electrical conductivity and the Seebeck effect in the spinel series  $Zn_{1-x}Cu_xCr_2Se_4$  in the whole range of concentrations as well as an attempt to evaluate both the carrier concentration and the mobility and the Fermi energy on the base of the theoretical considerations.

### 2. Experimental and results

The polycrystalline samples of  $Zn_{1-x}Cu_xCr_2Se_4$  with  $x = 0.0, 0.01, 0.02, 0.025, 0.05, 0.07, 0.1, 0.2, 0.3, 0.5, 0.7, 0.8, 0.9$  and  $1.0$  have been studied. The technology and the methods of the measurements of both the electrical conductivity and the Seebeck coefficient are described in [1, 6-8]. From the measurement of the electrical conductivity ( $\sigma$ ) and the Seebeck coefficient ( $\alpha$ ) it follows, that all the spinels under study are p-type semiconductors. The Seebeck coefficient decreases from  $451 \mu V/K$  at  $x = 0$  to  $17 \mu V/K$  at  $x = 1$ . For  $ZnCr_2Se_4$  the Seebeck coefficient increases almost linearly with temperature. For the samples with  $x \cong 0.3$  a change of the conductivity character from the semiconductive into metallic one is observed. The curves  $\ln \sigma$  vs.  $10^3/T$  reveal bends indicating clearly two values of the activation energy  $E$ , which was determined for each straight line part of the curve from the relation  $\sigma = \sigma_0 \exp(-E/kT)$  with the accuracy of  $\pm 0.0005$  eV.

### 3. Calculations

To calculate the concentration  $p$ , the mobility  $\mu$  and the Fermi energy  $E_F$  a procedure described in [9] was used with the following assumptions: a) the extrinsic conductivity is of one type (p-type); b) the Zn-vacancies make the acceptor levels (playing role of a double acceptor) [4]; c) there exist two independent acceptor levels with different activation energies ( $E_1$  and  $E_2$ ). Taking into account the well-known formulae for the hole concentration  $p$  in the valence band and for the concentration  $N_i$  of the acceptor levels filled doubly as well as assuming electrical neutrality  $p = N_i$  a 3rd order equation was obtained:

$$Ay^3 + By^2 + Cy + D = 0 \quad (1)$$

where:  $y = \exp[-E_F/kT]$ ,

$A, B, C, D$  – coefficients which are functions of  $E_1, E_2, N_d$  and  $N_s$ .

The values  $N_s$  and  $N_d$ , i.e. the concentrations of both the shallow and deep acceptor levels were determined from the condition:

$$\sigma(T)/\sigma(T_0) = p(T)/p(T_0) \quad (2)$$

where both  $p(T)$  and  $p(T_0)$  are functions of either ( $E_1, N_s$ ) or ( $E_2, N_d$ ), according to the corresponding straight line interval of the conductivity curve ( $\ln \sigma$  vs.  $10^3/T$ ) (see Tab. I). Solving the equation (1) with the use of the method described in [10] one comes to the following formulae:

$$p = N_v y_1 \quad (3)$$

$$\mu = \sigma / e N_v y_1 \quad (4)$$

$$E_F = kT \ln(1/y_1) \quad (5)$$

where:  $y_1$  – the only one positive solution of the equation (1),  $N_v$  – effective density of states of the valence band,  $e$  – elementary charge,  $k$  – Boltzmann constant. The results at 300 K are presented in figure 1. It turns out that: 1)  $\mu$  strongly increases with temperature for  $0.0 \leq x < 0.07$ ; 2)  $\mu(T) = \text{const}$  for  $x = 0.07$  and  $0.1$ ; 3)  $\mu$  decreases with the increase of tempera-

Table I. - Values of  $E_1$ ,  $E_2$ ,  $N_s$  and  $N_d$  for the spinels under study.

$x$	$E_1$ [eV]	$E_2$ [eV]	$N_d$ [ $m^{-3}$ ]	$N_s$ [ $m^{-3}$ ]
0.00	0.056	0.2	$1.2 \times 10^{21}$	$2.4 \times 10^{21}$
0.01	0.034	0.1	$1.8 \times 10^{23}$	$1.1 \times 10^{24}$
0.02	0.027	0.086	$2.6 \times 10^{23}$	$1.9 \times 10^{24}$
0.025	0.016	0.066	$3.2 \times 10^{23}$	$2.0 \times 10^{24}$
0.05	0.0071	0.045	$4.6 \times 10^{23}$	$2.6 \times 10^{24}$
0.07	0.0093	0.044	$7.0 \times 10^{23}$	$3.4 \times 10^{24}$
0.10	0.0084	0.057	$8.2 \times 10^{23}$	$5.4 \times 10^{24}$
0.20	0.0049	0.47	$9.0 \times 10^{23}$	$7.2 \times 10^{24}$
0.30	0.0033	-0.0004	$4.0 \times 10^{24}$	$1.2 \times 10^{25}$
0.50	-0.0049	-0.0241	$1.9 \times 10^{25}$	$7.8 \times 10^{25}$
0.70	-0.0046	-0.0224	$4.9 \times 10^{25}$	$1.7 \times 10^{26}$
0.80	-0.0044	-0.0305	$5.2 \times 10^{25}$	$2.4 \times 10^{26}$
0.90	-0.0027	-0.0211	$1.6 \times 10^{26}$	$5.0 \times 10^{26}$
1.00	-0.0025	-0.0271	$2.0 \times 10^{26}$	$5.8 \times 10^{26}$

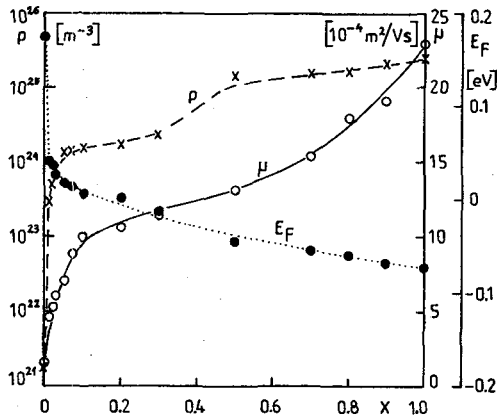


Fig. 1. - Dependence of  $p$ ,  $\mu$  and  $E_F$  on  $x$  at 300 K.

ture for  $x \geq 0.2$  and 4)  $p$  increases with temperature for all the samples under study, but the smaller  $x$  the stronger this dependence.

#### 4. Conclusions

The experimental results and the theoretical considerations suggest, that in the spinel series under study the changes of the electrical conductivity are linked

with both the changes of the concentration and the mobility of the current carriers. It testifies to that the two mechanisms are thermally activated. The increase of the hole concentration  $p$  and their mobility  $\mu$  with the increase of  $x$  (see Fig. 1) is connected - as it seems to us - with the increase of  $Cr^{4+}$  concentration, which is in the mixed chromium valence band ( $Cr^{3+}$ ,  $Cr^{4+}$ ) the main source of the concentration increase of the p-type current carriers. The Zn vacancies influence the hole concentration increase only for  $ZnCr_2Se_4$  and for the samples with small  $x$ . The value of  $E_F$ , calculated from equation (5), decreases with the increase of  $x$  (see Fig. 1), so that starting from  $x = 0.05$ , the inequality  $-5 kT < E_F < 1 kT$  is valid, which suggests, that these spinels are partially degenerated. This conclusion is confirmed also by the weak dependence of the hole concentration on temperature.

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