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Electrical and Magnetic Studies of $Zn_xMn_yCr_zSe_4$ *p*-Type Semiconductors

I. Jendrzejewska[a], T. Groń[b], H. Duda[b], P. Zajdel[b], A.W. Pacyna[c] and E. Maciążek[a]

[a]Institute of Chemistry, University of Silesia, Bankowa 14, 40-006 Katowice, Poland

[b]Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

[c]The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences Radzikowskiego 152, 31-342 Kraków, Poland

The structural, electrical and magnetic investigations carried out on the $Zn_xMn_yCr_zSe_4$ polycrystals with $y = 0.19$, 0.29 and 0.38 revealed the spinel structure with the Mn ions occupying tetrahedral sites, *p*-type conduction with polaronic transport at high temperatures and antiferromagnetic order with a Néel temperature of 20 K and a Curie–Weiss temperature of 103 K. With increasing Mn content in a sample both the effective magnetic moment and the re-entrant temperature increase while the first and second critical fields connected with a metamagnetic transition and the breakdown of the conical spin arrangement decrease, respectively. These results are interpreted in terms of giant cubic anisotropy as well as an effect of Mn impurities on the screw structure of $ZnCr_2Se_4$.

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1. Introduction

$ZnCr_2Se_4$ combines a cubic normal spinel with a screw spin structure below $T_N = 20$ K [1] and a *p*-type semiconducting behavior [2]. Manganese substituting zinc in the tetrahedral site as Mn^{2+} couples ferromagnetically with Cr^{3+} ions in the octahedral site [3]. However, for low Mn content the Mn–Cr exchange coupling is not so strong to produce serious change in magnetic properties below T_N [3]. Nevertheless, manganese affects Cr–Cr exchange interaction in the paramagnetic state inducing a large cubic magnetic anisotropy due to Cr^{3+} clusters formed around Mn impurities. When Mn was absent no anisotropy was observed in the magnetic torque measurements [4]. The neutron diffraction of $Zn_{0.98}Mn_{0.02}Cr_2Se_4$ carried out at finite temperature revealed also that thermally activated magnons reduce magnetization of Cr^{3+} which is modified by Mn substitution and for this sample a larger magnetic moment than that of pure $ZnCr_2Se_4$ at 4.2 K was observed [5].

The main purpose of this work is an attempt to study an influence of substitution of the Mn magnetic ions up to $y = 0.38$ in the tetrahedral sites of the spinel structure on the electrical and magnetic properties of the $Zn_xMn_yCr_zSe_4$ spinel series.

2. Experimental details

Powder samples of the $Zn_xMn_yCr_zSe_4$ spinel series were obtained by a ceramic method [6]. The X-ray diffraction was done with the aid of the SIEMENS D5000 diffractometer and the structure refinement was made by the Rietveld method. A precise atomic content determination of each sample made by the inductively coupled plasma-atomic emission spectrometry showed cation deficiency, i.e. $x + y + z < 3$ (see Table I). The temperature dependences of dc $\chi_\sigma(T)$ and ac $\chi_{ac}(T)$ mass susceptibilities, electrical conductivity $\sigma(T)$ and thermoelectric power $S(T)$ were measured using: (1) a Cahn automatic magnetic electrobalance of the Faraday type and a Lake Shore 7225 ac susceptometer/dc magnetometer, (2) a 4-point dc method, and (3) a differential method with the temperature gradient ΔT of about 5 K, respectively. The dc susceptibility was measured in the zero-field (ZFC) and field cooling (FC) modes in the temperature range 4.3–50 K and in applied external magnetic field $H = 100$ Oe. For electrical measurements the powder samples were compacted in disk form (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa and they were next sintered during 2 h at 473 K.

3. Results and discussion

The X-ray studies revealed a spinel cubic structure with the space group $Fd3m$ (No. 227). The anion positional parameter u slightly increases from 0.26002 for $y = 0.19$, via 0.26032 for $y = 0.29$ to 0.26039 for $y = 0.38$, indicating that the unit cells of the spinels under study are distorted. For the ideal spinel structure $u = 0.25$.

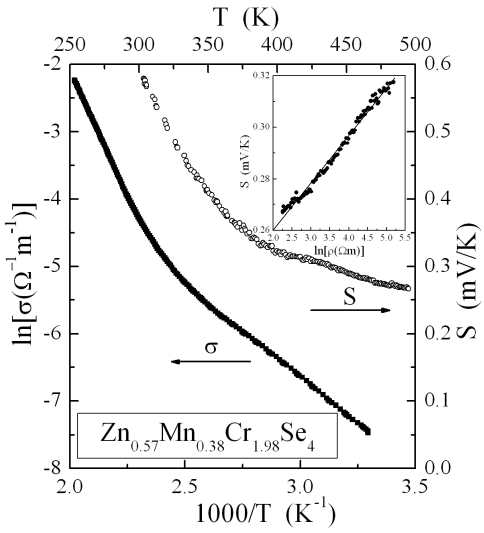

Fig. 1. The electrical conductivity ($\ln\sigma$) vs. reciprocal temperature T^{-1} and thermopower S vs. temperature T for $Zn_{0.57}Mn_{0.38}Cr_{1.98}Se_4$. Inset: thermopower S vs. electrical resistivity ($\ln\rho$). A linear regression is marked by a solid line.

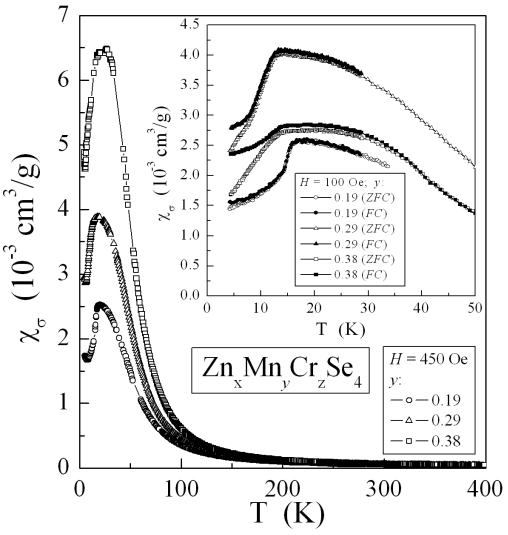

Fig. 2. The dc mass susceptibility χ_σ vs. temperature T for polycrystals with $y = 0.19$, 0.29 and 0.38 of the $Zn_xMn_yCr_zSe_4$ spinel system recorded at $H = 450$ Oe. Inset: ZFC and FC dc mass susceptibility χ_σ vs. temperature T recorded at $H = 100$ Oe.

TABLE I

The chemical composition of the $Zn_xMn_yCr_zSe_4$ spinels.

x	y	z	$x+y+z$
0.81	0.19	1.86	2.86
0.67	0.29	1.95	2.91
0.57	0.38	1.98	2.93

TABLE II

Magnetic parameters and critical fields H_{c1} and H_{c2} at 4.3, 10 and 15 K of the $Zn_xMn_yCr_zSe_4$ spinels for $y = 0.0$, 0.19, 0.29 and 0.38. T_N, θ_{CW} and T_{rsg} are the Néel, Curie–Weiss and re-entrant spin-glass temperatures, respectively, and μ_{eff} is the effective magnetic moment. For $ZnCr_2Se_4$ the relevant values were taken from Ref. [8].

Magnetic	Mn content y			
parameters	0.0	0.19	0.29	0.38
T_N [K]	21	20	17	23
θ_{CW} [K]	90	95	107	106
T_{rsg} [K]	12	15	20	35
μ_{eff} [μ_B/f.u.]	5.17	6.06	6.13	6.59
Critical fields	$T = 4.3$ K			
H_{c1} [kOe]	11	10	6	2
H_{c2} [kOe]	47	27	17	12
Critical fields	$T = 10$ K			
H_{c1} [kOe]	10	9.5	2.5	–
H_{c2} [kOe]	35	20	12	–
Critical fields	$T = 15$ K			
H_{c1} [kOe]	9	5	–	–
H_{c2} [kOe]	25	15	–	–

The Cr ions occupy the octahedral 16e sites, while the Zn and Mn ions are in the tetrahedral 4a positions. All the spinels under study are p-type thermally activated semiconductors. Figure 1 presents $\sigma(T)$ and $S(T)$ only for the sample with the highest Mn content. For the remaining samples these dependences are similar. In the inset of Fig. 1 the linear dependence between the thermopower (S) and the electrical resistivity ($\ln\rho$) is observed, suggesting a self-trapped or small polaron conduction [7] in the temperature range 400–500 K. The magnetic results depicted in Fig. 2 and in Table II revealed the antiferromagnetic order with the Néel temperature of 20 K and the Curie–Weiss temperature of 103 K. The effective magnetic moment μ_{eff} and the re-entrant temperature T_{rsg} increase with increasing Mn content. Below T_N the magnetic field dependence of susceptibility, $\chi_{ac}(H)$, shows two peaks. First peak at the critical field H_{c1}, connected with the breakdown of the helical spin structure [8], slightly decreases with temperature and stronger with Mn content. Second peak at the critical field H_{c2}, connected with the breakdown of the conical spin structure [8], drops strongly both with temperature and Mn content. For low Mn content both critical fields disappear at T_N while for higher — below T_N (Table II).

The magnetic results presented above show strong effect of Mn impurities both on T_{rsg} and a screw spin structure evidenced by the changes of H_{c1} and H_{c2}. As an explanation a coupling of distant cations by ferromagnetic superexchange interaction through valence band seems to

be reasonable [5]. In other words, the Cr–Mn exchange in the $Zn_xMn_yCr_zSe_4$ should be long range as Cr–Cr exchange in $ZnCr_2Se_4$ because, generally, in magnetic semiconductors electrons are not in localized state but in the Bloch orbitals [5]. In our case a hole transport via cation vacancies below 300 K dominates, because all samples have cation deficiencies and an increase of thermopower as temperature decrease is expected (see Fig. 1). Additionally, at high temperatures a polaron mechanism of the electronic transport occurs because the spinel unit cell is distorted ($u > 0.25$) and the carrier with its associated crystalline distortion is comparable in size to the cell parameter giving so-called a small, or Holstein, polaron. Moreover, with increasing Mn content the ZFC–FC splitting extends far above T_N (see inset in Fig. 2). It means that the giant cubic anisotropy connected with Cr^{3+} spin clusters formed around Mn impurities can affect the behavior of rather distant Cr spins in the paramagnetic state [4].

In conclusion, substitution of the Mn ions instead of Zn ones causes an increase of the effective magnetic moment, extends the re-entrant spin-glass state far above the ordering temperature, decreases strongly the critical fields, and finally, reveals a polaronic mechanism of the electrical conductivity at high temperatures.

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