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Effect of cation substitution on electrical conduction of the n-type $Zn_xSn_yCr_zSe_4$ spinels

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ABSTRACT

The electrical and magnetic measurements showed that the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinels are n-type semiconductors and antiferromagnets with the Néel temperature of 18.6 and 19.8 K, respectively. The $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinel has both higher effective magnetic moment and electrical conductivity, and lower activation energy in comparison with the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ one. It means that in the latter case the non-magnetic Sn ions (spin defects) in the octahedral coordination cause a narrowing of the majority spin t_{2g} orbital of the Cr^{3+} band leading to the lowering of the Fermi level accompanied with an increase of an energy gap. Comparable values of the Néel and Curie–Weiss temperatures in both cases suggest that the small content of the substituted Sn ions (5%) does not significantly influence on strength of the long- and short-range magnetic interactions.

1. Introduction and experimental

Much information has appeared in the literature on the magnetic and electrical properties of the spinels basing on the $ZnCr_2Se_4$ compound as a matrix. These spinels are either metals or semiconductors, either ferromagnets or antiferromagnets, and finally either ferrimagnets or Landau and Pauli paramagnets. The $ZnCr_2Se_4$ spinel shows the p-type semiconducting properties and a helical antiferromagnetic (AFM) spin structure below the Néel temperature $T_N \approx 20$ K with a strong ferromagnetic (FM) component evidenced by a large positive Curie–Weiss (CW) temperature of 115 K [1,2]. The helical structure has a FM arrangement in the (0 0 1) planes with a turning angle of 42° between the spins in adjacent (0 0 1) planes. The transition to the AFM state at T_N is accompanied by structural transformation from cubic $Fd\bar{3}m$ to tetragonal $I4_1/amd$ symmetry with a small contraction along the *c*-axis [3], although the latest structural investigations using synchrotron radiation defined this latter symmetry as orthorhombic *Fddd* [4]. It is well known from literature that a lot of magnetically ordered chromium spinels manifest structural instabilities which do not originate from a conventional Jahn–Teller instability, as the half-filled t_{2g} ground state of the Cr^{3+} ions is orbitally non-degenerative [5]. Another source of the structural instability is a competition between FM and AFM exchange of nearly equal strength yielding strong bond frustration as it was identified in AFM $ZnCr_2S_4$ [6]. A detailed latest investigation of $ZnCr_2Se_4$ single crystal [5] revealed the AMF order at $T_N = 21$ K with a positive CW temperature $\theta_{CW} = 90$ K, a metamagnetic transition at a critical field H_{c1} of about 10 kOe for $T = 2$ K connected with a simple spiral spin arrangement, the breakdown of the conical spin arrangement at the critical field H_{c2} of about 65 kOe for $T = 2$ K, the full saturation magnetisation of about 3 μ_B per Cr ion above H_{c2} for the FM spin arrangement and thermal expansion by external magnetic fields suggesting a spin-driven origin of the structural transformation.

Polycrystalline samples $Zn_xSn_yCr_zSe_4$ were obtained from the binary selenides (ZnSe, SnSe and Cr_2Se_3). They were prepared

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Table 1
Structural parameters obtained from the Rietveld refinement for $Zn_xSn_yCr_zSe_4$ series.

Spinel	$(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_{4.00}$	$Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_{4.00}$
a (pm)	1050.42(1)	1050.67(3)
u	0.25932(16)	0.25944(16)
R_F (%)	3.90	3.94
R_{Bragg} (%)	5.36	5.61
R_{wp} (%)	11.6	11.6
χ^2	1.28	1.33
U_{iso} (Å^2): Se	0.0042	0.0038
B_{aniso} (Å^2): Se	$B_{11} = B_{22} = B_{23} = 0.000749(3)$, $B_{12} = B_{13} = B_{23} = -0.00030(4)$	$B_{11} = B_{22} = B_{23} = 0.00068(4)$, $B_{12} = B_{13} = B_{23} = -0.0025(5)$
U_{iso} (Å^2): Zn/Sn; Zn	0.0063	0.0025
B_{aniso} (Å^2): Zn/Sn; Zn	$B_{11} = B_{22} = B_{23} = 0.00112(0)$	$B_{11} = B_{22} = B_{23} = 0.00045(0)$
U_{iso} (Å^2): Cr; Cr/Sn	0.0027	0.0047
B_{aniso} (Å^2): Cr; Cr/Sn	$B_{11} = B_{22} = B_{23} = 0.000479(6)$, $B_{12} = B_{13} = B_{23} = -0.00002(9)$	$B_{11} = B_{22} = B_{23} = 0.00084(6)$, $B_{12} = B_{13} = B_{23} = -0.0024(10)$

Note: R_F, R_{Bragg}, R_{wp} and χ^2—criteria of fit [7], a and u are the lattice and anion positional parameters, U_{iso} and B_{aniso} are the isotropic and anisotropic displacement parameters, () and [] brackets mean tetra- and octahedral positions of Sn ions in the spinel structure, respectively. Atomic positions are given in standard setting for space group No. 227: Zn 8a (1/8, 1/8, 1/8), Cr 16d (0.5, 0.5, 0.5), Se 32e (u, u, u).

by annealing stoichiometric mixtures of the elements: Zn, Sn, Cr and Se with 5N purity. The mixtures were pulverised in an agate mortar in stoichiometric quantities and sealed in fused silica ampoules evacuated to a pressure of about 10^{-5} Torr. The samples were sintered three more times at 1073 K for 198 h. After the last sinter, the samples were quenched in water with ice. The X-ray powder diffraction data of polycrystalline samples were collected using a Philips X-Pert (PW3050) diffractometer (Cu Kα radiation ($\lambda_1 = 1.54056$ and $\lambda_2 = 1.54443$ Å) over an angular range of 2θ: 10–135°). In order to determine phase composition and refinement structure a Rietveld method was used (Table 1). Chemical compositions of the spinels under study were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES) method. The molar fractions of constituent elements obtained with this procedure were finally normalised to the selenium nominal stoichiometry. The resulting compositions were found to be $Zn_{0.87}Sn_{0.043}Cr_{2.02}Se_{4.00}$ for nominal $Zn_{0.9}Sn_{0.1}Cr_2Se_4$ and $Zn_{0.93}Cr_{1.95}Sn_{0.05}Se_{4.00}$ for nominal $ZnCr_{1.9}Sn_{0.1}Se_4$ (Table 2).

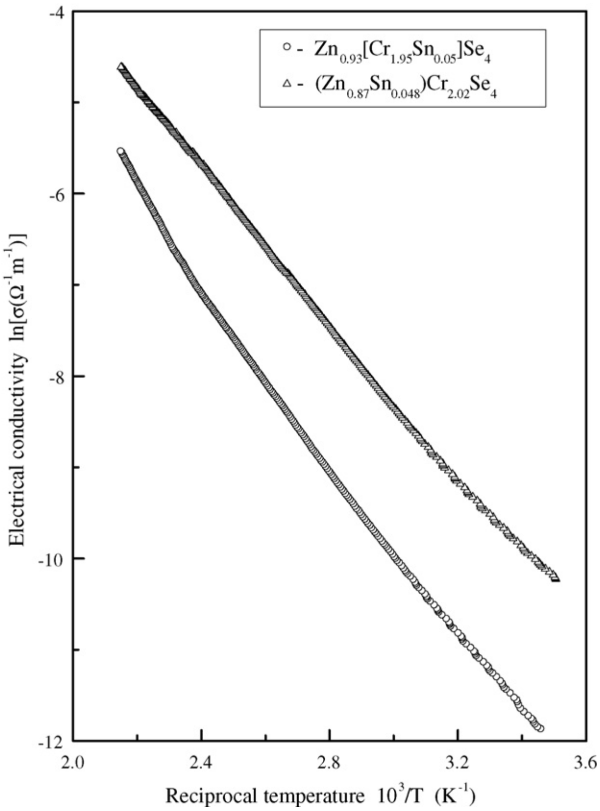

Fig. 1. Electrical conductivity $\ln\sigma$ vs. reciprocal temperature T^{-1} of the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinels.

The mass susceptibility $\chi_\sigma(T)$, electrical conductivity $\sigma(T)$ and thermopower $S(T)$ measurements were carried out on the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinels using a: (1) Cahn automatic magnetic electrobalance of the Faraday type in the temperature range 4.2–350 K and in applied external field $H = 700$ Oe. A correction for diamagnetic contribution has been taken into account [8] and the Curie–Weiss law was fitted by adding a temperature independent residual susceptibility χ_0 (Table 2), (2) 4-point dc method for $\sigma(T)$ in the temperature range 280–480 K using a semi-automatic bridge [9] containing the CA3160 integral circuit with the input impedance of 1.5 TΩ and the HP 34401A digital multimeters controlled by the computer and LabView® commands. The maximal error $\delta\sigma/\sigma$ was less than ±1%. The activation energy E_A and the temperature coefficient of resistivity α_{TCR} were determined from the formulas $\sigma = \sigma_0 \exp(-E_A/kT)$ and $\rho = \rho_0(1 + \alpha_{TCR}\,\Delta T)$, respectively, and (3) differential method [10] in the temperature range 280–480 K with the temperature gradient $\Delta T \approx 5$ K. The accuracy of the value of thermopower was estimated to be better than 3 μV/K. For electrical measurements the powder samples were compacted in disc form (10 mm in diameter and 1–2 mm thick) using a pressure of 1.5 GPa and they were next sintered through 2 h at 200 K.

Table 2
Chemical composition of $Zn_xSn_yCr_zSe_4$ spinels made by the ICP-AES method.

Nominal composition	Zn		Sn		Cr		Se		Measured composition
	% weight	s	% weight	s	% weight	s	% weight	s	
$Zn_{0.9}Sn_{0.1}Cr_2Se_4$	12.46	0.22	1.31	0.04	21.95	0.11	64.28	2.22	$(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_{4.00}$
$ZnCr_{1.9}Sn_{0.1}Se_4$	12.61	0.49	1.22	0.06	20.95	0.52	65.22	1.07	$Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_{4.00}$

Note: s is the standard deviation.

Table 3
Magnetic and electrical parameters of the spinels with tetra- and octahedral coordination of Sn ions.

Spinel	μ_{eff} (μ_B/f.u.)	C_M (K cm^3/g)	T_N (K)	θ_{CW} (K)	χ_0 (cm^3/g)	E_A (eV)	α_{TCR} ($\times 10^{-3}$ K^{-1})
$(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_{4.00}$	5.92	9.07×10^{-3}	19.8	58	-10.45×10^{-7}	0.29	−31.6
$Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_{4.00}$	5.77	8.60×10^{-3}	18.6	61	-8.207×10^{-7}	0.34	−36.4

Note: μ_{eff} is the effective magnetic moment, C_M is the Curie constant, T_N and θ_{CW} are the Néel and Curie–Weiss temperatures, respectively, χ_0 is the temperature independent residual susceptibility, E_A is the activation energy at 300 K and α_{TCR} is the temperature coefficient of resistivity at 300 K.

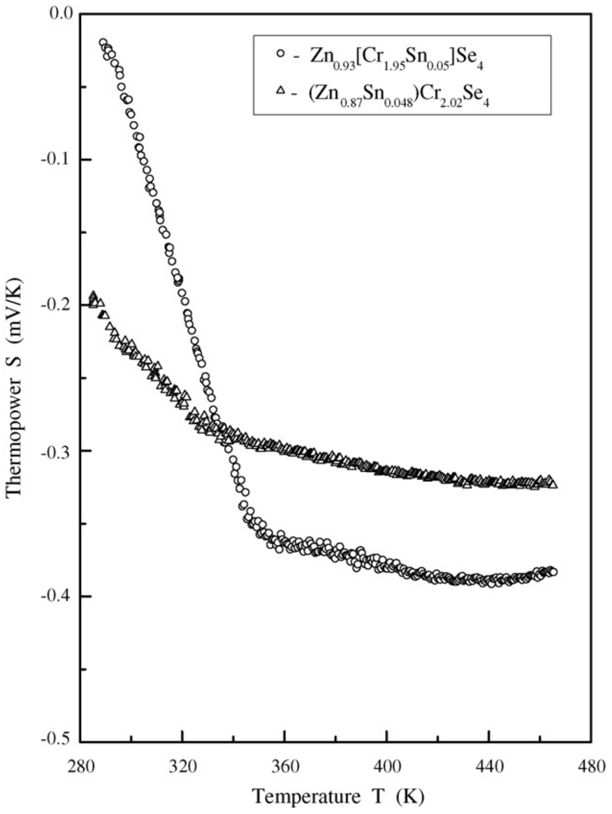

Fig. 2. Thermopower S vs. temperature T of the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinels.

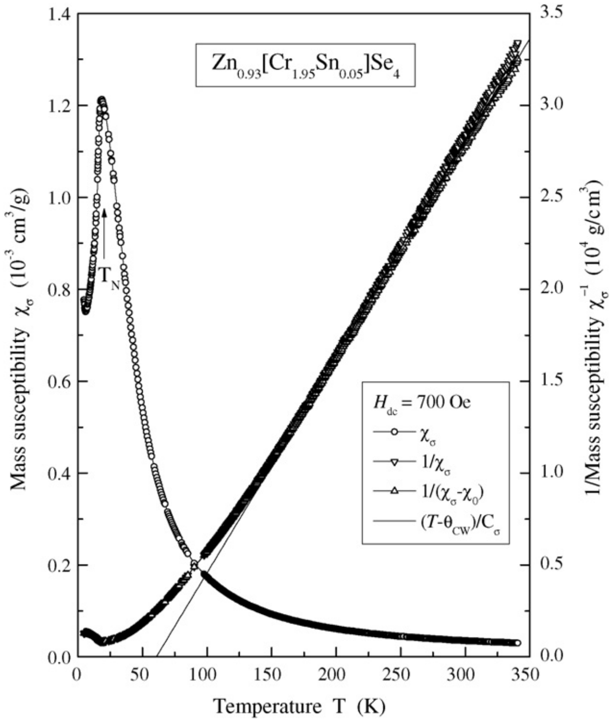

Fig. 3. Mass susceptibility χ_σ and $1/\chi_\sigma$ vs. temperature T of the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ spinel at 700 Oe.

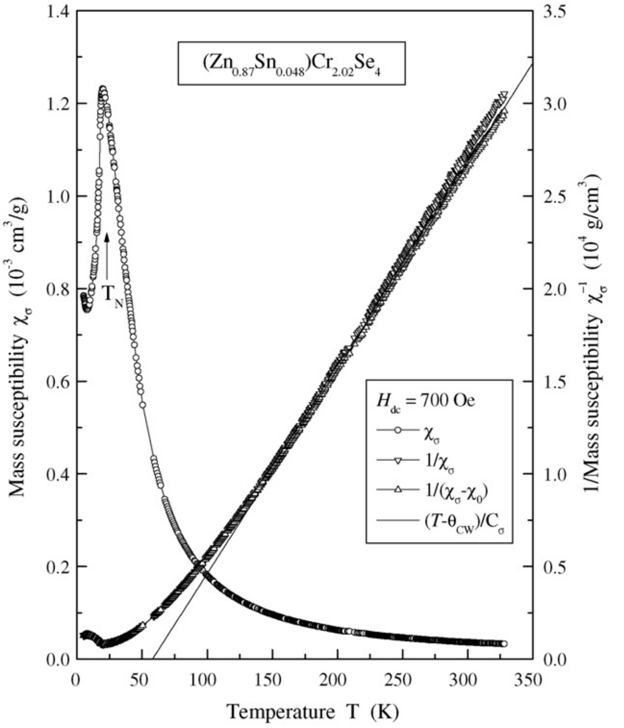

Fig. 4. Mass susceptibility χ_σ and $1/\chi_\sigma$ vs. temperature T of the $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinel at 700 Oe.

The present contribution reports the X-ray diffraction data, electrical and magnetic properties for two representative compositions doped with low content of the Sn ions ($y \leq 0.05$) located both in tetra- and octahedral sites of the spinel structure. It was thus natural to expect the low conductivity (typical of dielectrics) in the case of the antiferromagnetic spin arrangement of the magnetic moments.

2. Results and discussion

The structural, compositional, electrical and magnetic results are presented in Tables 1–3 and in Figs. 1–4. The lattice parameter is slightly larger and the anion positional parameter is slightly smaller in comparison with a pure $ZnCr_2Se_4$ spinel (a = 1049.4 pm [11], u = 0.2599 [12]) indicating that the unit cells of the spinels under study are less distorted. For the ideal spinel structure u = 0.25 [13,14]. A Rietveld refinement shows both tetra- and octahedral coordination of the Sn ions, which is additionally confirmed by the values of the effective magnetic moment μ_{eff} (Table 3) in comparison with the theoretical one of 6 μ_B per formal unit. Coordination of the Sn ions in amount of about 5% does not significantly influence on the magnetic properties of the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinels. They are antiferromagnets with a Néel temperature of 19 K and a Curie–Weiss temperature of 60 K (Table 3). The long-range antiferromagnetic superexchange interaction is slightly weakened while the short-range ferromagnetic exchange interaction is strongly lowered in comparison with the magnetic interactions of the pure $ZnCr_2Se_4$ spinel [1,2,5]. An essential difference between spinels under study and the $ZnCr_2Se_4$ one concerns the electrical properties. The $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinels have low n-type electrical conductivity typical for dielectrics with strong thermal activation (large E_A and α_{TCR} at 300 K, see Table 2). Its value is almost four orders of magnitude smaller in comparison with the p-type conduction of $ZnCr_2Se_4$ at room temperature [15]. Moreover, the electrical conductivity of the $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ spinel with octahedral coordination of the Sn ions is about one order of magnitude smaller than the electrical conductivity of the $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ one with tetrahedral coordination of the Sn ions. This effect one can explain in a framework of the quantum band model which predicts a lowering of the Fermi level in the lowest Cr^{3+} Mott–Hubbard subband of $3d^3$ t_{2g} narrowed band giving an increase of the energy gap, when the Sn^{3+} ions (spin defects) are substituted in the octahedral sites instead of Cr^{3+} ones. A nature of the n-type conductivity in this case may originate from selenium deficiencies, too, as the slight non-stoichiometry is observed. Higher electrical conduction in $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinel is connected with the fact that the Sn^{3+} ions located in the tetrahedral sites induce the Cr^{2+} ions, leading to the hopping process involving a transfer of electrons from Cr^{2+} to Cr^{3+} in the extremely mixed valence narrow band.

The susceptibility curves on Figs. 3 and 4 reveal besides a peak at ordering temperature T_N, where the helical spin arrangement breakdowns, also a minimum at 6.2 K for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and at 7.9 K for $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$. Anomaly behaviour of susceptibility below T_N may suggest a rearrangement of the spin structure connected with a Landau contribution to the total susceptibility as the temperature independent residual susceptibility χ_0 is negative (Table 3). Thus, it leads to the weakness of the simple spin spiral ordered antiferromagnetically, simultaneously, strengthening a ferromagnetic coupling in the (0 0 1) planes of the spinel structure. Experiment shows also that a parallel spin coupling exists in the ferromagnetic clusters above the ordering temperature T_N.

In conclusion, a slight Sn-doping of the $ZnCr_2Se_4$ makes a spinel structure more ideal, simultaneously, causing a drastical decrease of the electrical conduction typical for dielectrics accompanied by the antiferromagnetic spin arrangement of the magnetic moments.

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