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Electrical and Magnetic Characterization of $ZnCr_{2-x}V_xSe_4$ Spinel Semiconductors

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Single crystals of $ZnCr_2Se_4$ spinel doped with vanadium were prepared by chemical vapour transport. The chemical compositions of three crystals have been determined by X-ray diffraction. The structure refinement using the SHELXL-93 program system determine the cation distribution in the system as $ZnCr_{2-x}V_xSe_4$. For x values equal to 0.03, 0.1 and 0.13 the observed symmetry was cubic, space group $Fd3m$. Based on the structural data, influence of the V ions on the magnetic and electrical properties has been analyzed.

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1. Introduction

$ZnCr_2Se_4$ belongs to the group of normal spinels with Zn^{2+} located at tetrahedral (A) sites and Cr^{3+} occupying octahedral (B) sites of the cubic close-packed array of selenium anions [1]. This spinel reveals an aniferromagnetic order with the Néel temperature $T_N = 21$ K and strong ferromagnetic exchange evidenced by a large positive value of the Curie–Weiss temperature $\theta_{CW} = 115$ K [2]. The sharp anomalies in the specific heat and thermal expansion indicated first order magnetic phase transitions [3]. At room temperature $ZnCr_2Se_4$ is semiconductor with a magnetic spiral structure with the angle $\varphi = 42 \pm 1°$ [2]. The magnetic properties result from the nearest-neighbour ferromagnetic Cr–Cr interactions in the $\langle 001 \rangle$ planes and the more distant superexchange antiferromagnetic Cr–Se–Cr interactions between these planes. In this paper we report results of structural, magnetic and electric studies of single crystals of the $ZnCr_{2-x}V_xSe_4$ spinel system.

2. Experimental details

Detailed structural, electrical and magnetic investigations were carried out on single-crystalline $ZnCr_{2-x}V_xSe_4$ spinels with $x = 0.03$, 0.1 and 0.13. The structure refinement was done using the SHELXL-93 program system [4] showing that all single crystals under study have cubic structure with the space group $Fd3m$ (No. 227). The Cr and V ions occupy the octahedral 16e sites, while the Zn ions are in the tetrahedral 4a positions. The crystal data are summarized in Table I, together with results of the structure refinement. The temperature measurements of mass susceptibility $\chi_\sigma(T)$ were made with the aid of the Faraday type Cahn RG automatic electrobalance in the temperature range 4.2–300 K and in applied external magnetic field $H_{dc} = 919$ Oe. The temperature dependences of electrical conductivity $\sigma(T)$ and thermoelectric power $S(T)$ were measured using a 4-point dc method and a differential method with the temperature gradient ΔT of about 5 K, respectively. The magnetic and electrical data are depicted in Figs. 1–3 and summarized in Table II.

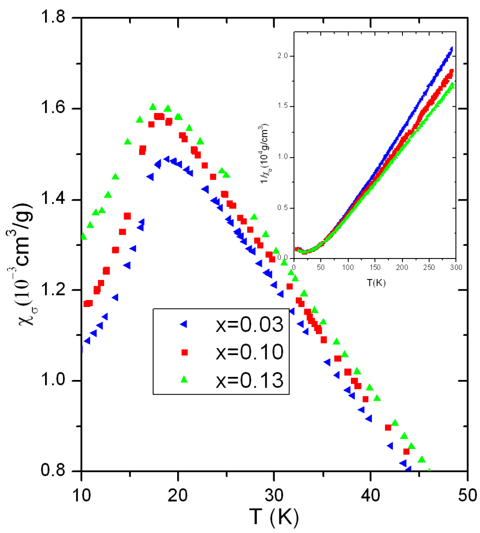

Fig. 1. The dc mass susceptibility χ_σ vs. temperature T for single crystals with $x = 0.03$, 0.1, 0.13 of the $ZnCr_{2-x}V_xSe_4$ spinel system recorded at $H = 919$ Oe. Inset: inverse susceptibility versus T at 919 Oe indicating Curie–Weiss behavior.

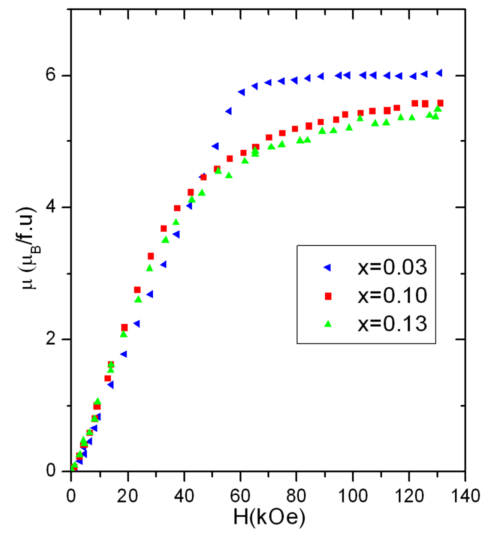

Fig. 2. Magnetic moment μ vs. magnetic field H for $ZnCr_{2-x}V_xSe_4$.

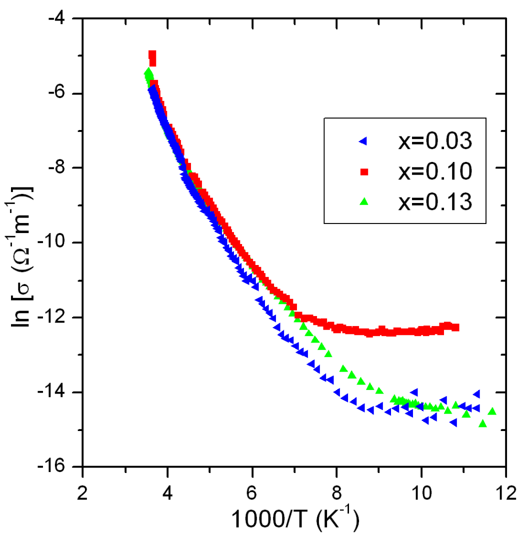

Fig. 3. Electrical conductivity σ vs. reciprocal temperature T^{-1} for $ZnCr_{2-x}V_xSe_4$.

3. Results and discussion

The electrical and magnetic measurements showed that the spinels under study are antiferromagnets and semiconductors with thermally activated electron transport. With increasing V content both T_N and θ_{CW} slightly decrease. It means that short interactions weaken, ferromagnetic weaken more than antiferromagnetic one. These results well correlate with the energy activation electrical conductivity and with the fact that magnetization does not reach at saturation for single crystal with higher V content. Comparable values of electrical conductivity and positive values of thermopower seem to be connected with thermally activated hopping of electrons via cation vacancies, plays the rule of acceptors, in the forbidden gap.

TABLE I

Structural parameters of the $ZnCr_{2-x}V_xSe_4$ spinel system. a and u are the lattice and anion positional parameters, respectively, R_1 and wR_2 — criteria of fit.

x	0.03	0.1	0.13
a [pm]	1049.315(16)	1049.926(17)	1050.351(15)
u	0.25934(1)	0.25932(2)	0.25931(2)
R_1	0.0185	0.0308	0.0313
wR_2	0.0431	0.0761	0.0816
Bond angles in degs between anions and cations			
Zn	109.47(0)	109.47(0)	109.47(0)
V/Cr	85.48(1)	85.48(7)	85.48(1)
V/Cr	94.52(1)	94.52(7)	94.52(1)
V/Cr	180.00(0)	180.00(0)	180.00(0)
Distances in pm between anions and cations			
Zn	244.16(2)	244.26(4)	244.34(4)
V/Cr	252.91(1)	253.08(2)	253.19(2)

TABLE II

Electrical and magnetic parameters of the $ZnCr_{2-x}V_xSe_4$ spinel system. μ_{eff} is the effective magnetic moment, C_σ is Curie constant, χ_0 is the temperature independent diamagnetic contribution to the total susceptibility, T_N and θ_{CW} are the Néel and Curie–Weiss temperatures, respectively, σ is the electrical conductivity, E_A is the activation energy and S is the thermopower at 300 K.

x	0.03	0.1	0.13
μ_{eff} [μ_B/f.u.]	6.70	7.18	7.61
C_σ [K cm^3/g]	1.157×10^{-2}	1.328×10^{-2}	1.492×10^{-2}
χ_0 [cm^3/g]	-9.562×10^{-6}	-4.570×10^{-6}	-2.228×10^{-6}
T_N [K]	19.0	17.8	17.5
θ_{CW} [K]	53	46	38
σ [Ω^{-1} m^{-1}]	8.3×10^{-3}	5.5×10^{-2}	9.8×10^{-3}
E_A [eV]	0.21	0.24	0.25
S [μV/K]	215	500	420

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