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Effect of Cation Substitution on Critical Fields in the n-type $Zn_xSn_yCr_zSe_4$ Spinel Semiconductors

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The ac dynamic magnetic susceptibility was used to study a cation substitution on critical fields in polycrystalline $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ spinels with tetra- and octahedral coordination of Sn ions, respectively. An increasing static magnetic field shifts the Néel temperature T_N to lower temperatures while a susceptibility peak at T_m in the paramagnetic region — to higher temperatures. Below T_N the magnetic field dependence of susceptibility, $\chi_{ac}(H)$, shows two peaks at critical fields H_{c1} and H_{c2}. The values of H_{c1} decrease slightly with temperature while the values of H_{c2} decrease strongly with temperature, especially for spinel with octahedral coordination of Sn ions, suggesting a weakness of the ferromagnetic component.

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1. Introduction

Previous structural, electrical and magnetic investigations [1] carried out on the $ZnCr_2Se_4$ spinel doped with low content of the Sn ions ($y \leq 0.05$) located both in tetra- and octahedral sites of the spinel structure revealed the n-type semiconducting properties and antiferromagnetic order. In particular, the $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinel has higher both 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 (see Table I). Higher electrical conduction of $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinel was explained by the fact that the Sn^{3+} ions located in the tetrahedral sites may 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. On the other hand, lower electrical conduction of $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ spinel was considered in the framework of the quantum band model which predicts a lowering of the Fermi level in the lowest Cr^{3+} Mott–Hubbard sub-band of $3d^3t_{2g}$ narrowed band giving a larger energy activation (see Table I) and consequently a larger value of the forbidden band, when the Sn^{3+} ions (spin defects) occupy the octahedral sites instead of Cr^{3+} ones [1].

Pure $ZnCr_2Se_4$ as a matrix combines a p-type semiconducting behaviour of the Arrhenius type and antiferromagnetic order with the Néel temperature $T_N = 20$ K and the Curie–Weiss temperature $\theta_{CW} = 115$ K [2, 3].

TABLE I

Structural, magnetic and electrical parameters of the $Zn_xSn_yCr_zSe_4$ spinels with tetra- $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ — A and octahedral $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ — B coordination of Sn ions [1]. a and u are the lattice and anion positional parameters, respectively, μ_{eff} is the effective magnetic moment, 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.

Parameters	A	B
a [pm]	1050.42(1)	1050.67(3)
u	0.25932(16)	0.25944(16)
μ_{eff} [μ_B/f.u.]	5.92	5.77
T_N [K]	19.8	18.6
θ_{CW} [K]	58	61
σ [Ω^{-1} m^{-1}]	6.56×10^{-5}	1.0×10^{-5}
E_A [eV]	0.29	0.34
S [μV/K]	−227	−69

2. Experimental details

The ac susceptibility (i.e., a modulus of its real and imaginary part) vs. external magnetic field up to 60 kOe was measured at three different temperatures in the range of magnetic ordering and at internal oscillating magnetic field $H_{ac} = 1$ Oe with internal frequency $f = 120$ Hz using a Lake Shore 7225 ac susceptometer. The ac susceptibility vs. temperature was recorded at $H_{ac} = 1$ Oe with $f = 120$ Hz for external magnetic fields $H = 0$ and 50 kOe.

3. Results and discussion

The magnetic field dependence of susceptibility, $\chi_{ac}(H)$, shows two peaks below the Néel temperature T_N (see Figs. 1 and 2 and Table II).

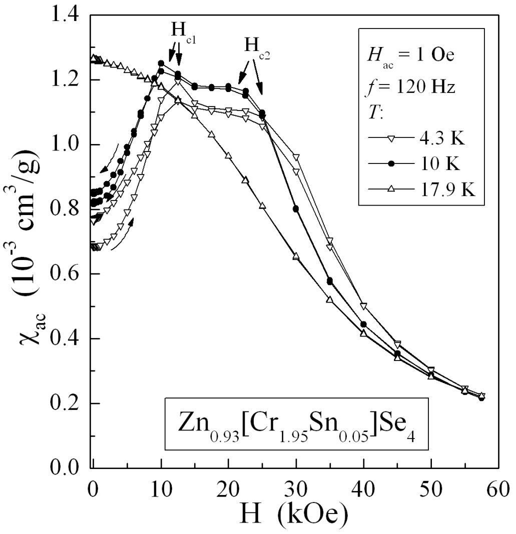

Fig. 1. Ac mass susceptibility χ_{ac} vs. external magnetic field H for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$. The critical fields H_{c1} and H_{c2} and a run of magnetic field are indicated by arrows.

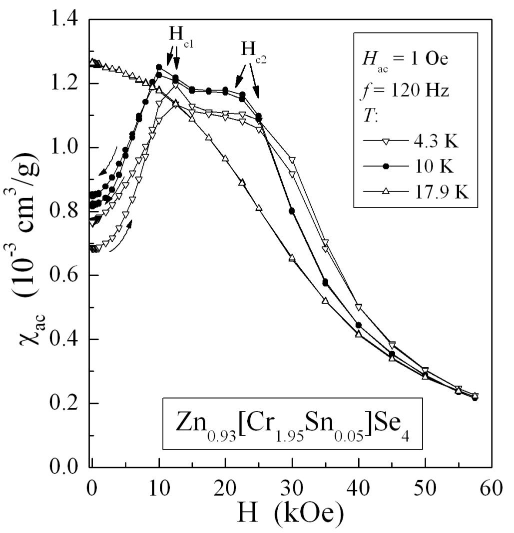

Fig. 2. As in Fig. 1 but for $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$.

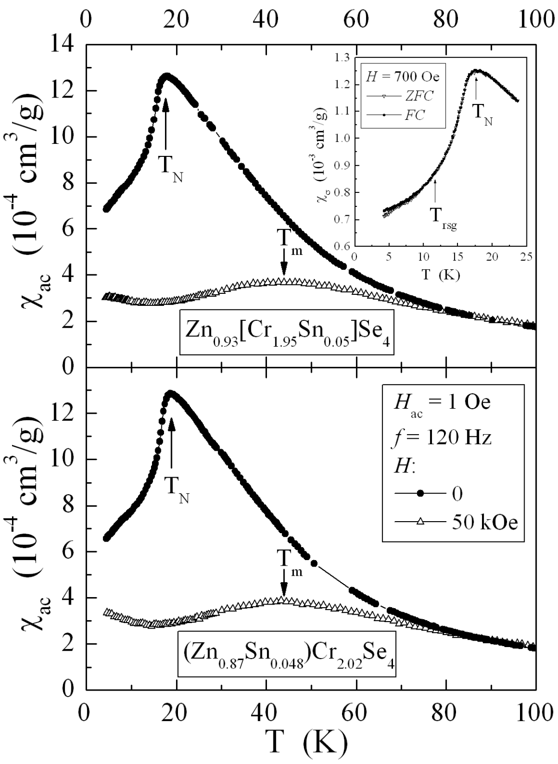

Fig. 3. Ac mass susceptibility χ_{ac} vs. temperature T for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$ and $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ spinels. Inset: ZFC and FC dc mass susceptibility χ_σ vs. temperature T for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$. The T_N, T_m and T_{rsg} temperatures are indicated by arrows.

TABLE II

Critical fields H_{c1} and H_{c2} at 4.3 and 10 K of the $Zn_xSn_yCr_zSe_4$ spinels. T_{rsg} is the re-entrant spin-glass temperature and T_m corresponds to the maximum of ac susceptibility in the paramagnetic region. Experimental data for $ZnCr_2Se_4$ were taken from Ref. [5] for comparison. A and B are defined as in Table I.

Spinel	$ZnCr_2Se_4$	A	B
T_{rsg} [K]	12	12	12
T_m [K]	43.5	42.9	43.1
$T = 4.3$ K			
H_{c1} [kOe]	10	12	12
H_{c2} [kOe]	48	32	25
$T = 10$ K			
H_{c1} [kOe]	8.6	10	10
H_{c2} [kOe]	35	25	21

First, at the critical field H_{c1}, connected with a metamagnetic transition and the breakdown of the helical spin structure, which slightly decreases with temperature. Second, at the critical field H_{c2}, connected with the breakdown of the conical spin structure, which drops strongly with temperature. The latter is mainly responsible for a spin frustration of the re-entrant type confirmed by the experimentally observed splitting of the zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities at a re-entrant spin-glass temperature, T_{rsg}, well below the ordering temperature, T_N (see the inset of Fig. 3). At T_N both critical fields disappear.

A change of Sn position from tetra- to octahedral site leads to the lowering of the H_{c2}, while the H_{c1} remains almost unchanged (see Table II). It means that the non--magnetic Sn ions weaken the ferromagnetic short-range interactions in the (001) planes, while the long-range antiferromagnetic exchange interactions between the spins in adjacent (001) planes [3] remain still strong. Additionally, at magnetic field of 50 kOe a shift of T_N below 4.3 K and an appearance of the maximum of ac susceptibility at T_m in the paramagnetic region were observed (see Fig. 3 and Table II), suggesting that the short-range magnetic interactions exist in the ferromagnetic clusters above ordering temperature. Similar behaviour has been observed in the $Zn_xCr_yAl_zSe_4$ spinel series [4].

Comparing the values of the critical fields of the spinels under study with the relevant ones of $ZnCr_2Se_4$ matrix [5] one can conclude that the values of H_{c1} are of the same order, while the values of H_{c2} rapidly decrease with Sn-substitution, especially, when the Sn-ions occupy the octahedral sites in the spinel structure (see Table II). A such drastical lowering of the second critical field may be connected with the cation deficiencies ($x + y + z < 3$) observed in both compounds, and the sum of $x + y + z$ is: 2.938 for $(Zn_{0.87}Sn_{0.048})Cr_{2.02}Se_4$ and 2.93 for $Zn_{0.93}[Cr_{1.95}Sn_{0.05}]Se_4$.

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