Influence of Temperature on Critical Fields in Zn$_x$Sb$_y$Cr$_z$Se$_4$

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1. Introduction

Previous structural and magnetic investigations carried out on the ZnCr$_2$Se$_4$ spinel doped with the Sb ions up to 0.2 located in tetrahedral sites of the spinel structure revealed the antiferromagnetic order with the Néel temperature $T_N = 22$ K and the strong short-range ferromagnetic exchange evidenced by the large and positive value of the Curie–Weiss temperature $\theta_{CW} = 106$ K [1]. The magnetic moment taken from experiment is quite close to the spin-only value for Cr$^{3+}$. Chemical composition of the Zn$_x$Sb$_y$Cr$_z$Se$_4$ single crystals was determined by the non-destructive energy-dispersive X-ray fluorescence spectrometry showing a slight non-stoichiometry in the octahedral sites [1]. The structure refinement performed by the SHELXL-97 program package revealed that all single crystals under study have cubic structure with the space group Fd$ar{3}$m (No. 227). The Cr and ions occupy the octahedral 16e sites, while the Zn and Sb ions are in the tetrahedral 4a positions [1]. The structural and magnetic parameters are displayed in Table I.

2. Experimental details

The ac susceptibility $\chi_{ac}$ vs. external magnetic field up to 60 kOe was measured at 4.3, 8, 12, 18, 21.2 and 22.8 K at internal oscillating magnetic field $H_{ac} = 1$ Oe with internal frequency $f = 120$ Hz using a Lake Shore 7225 ac susceptometer. The $\chi_{ac}$ vs. temperature was recorded at $H_{ac} = 1$ Oe with $f = 120$ Hz for external magnetic fields $H = 0$, 5, 12.5, 25, 40 and 50 kOe.

The electrical measurements have been done in the temperature range 270–500 K and in the (001) direction. The electrical conductivity $\sigma(T)$ has been measured with the aid of the 4-point dc method. The maximal error $\delta \sigma/\sigma$ was less than ±1%. The thermopower $S(T)$ was measured with a differential method using the temperature gradient $\Delta T$ of about 2 K. The accuracy of $S(T)$ was better than 3 $\mu$V/K.

![Table I](https://example.com/table1.png)

Structural and magnetic parameters of Zn$_x$Sb$_y$Cr$_z$Se$_4$. $a$ and $u$ are the lattice and anion positional parameters, $R_1$ and $wR_2$ – criteria of fit, $T_N$ is the Néel temperature, $\theta_{CW}$ is the Curie–Weiss temperature, $\mu_{\text{eff}}$ and $\mu_s$ are the effective and saturation magnetic moments, respectively [1].

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3. Results and discussion

The electrical results presented in Figs. 1 and 2 show the thermally activated p-type $\text{Zn}_x\text{Sb}_y\text{Cr}_z\text{Se}_4$ semiconductors of the Arrhenius type. A general decrease of thermopower below 400 K as well as an increase of the p-type electrical conductivity as the Sb content $y$ increases seem to be connected both with a hole transport in the lowest $\text{Cr}^{3+}d^2(t_2g^0)$ band and an activation of the holes in the valence band to the acceptor energy levels. The nature of acceptor levels can be related to the Cr vacancies, occupying the octahedral sites, because a slight increase of non-stoichiometry as the Sb content $y$ increases is observed (see Table I).

![Fig. 1](image1.png)  
**Fig. 1.** The electrical conductivity ($\ln \sigma$) vs. reciprocal temperature $T^{-1}$ for single crystals with $y = 0.11$, 0.16, and 0.20 of the $\text{Zn}_x\text{Sb}_y\text{Cr}_z\text{Se}_4$ spinel system.

![Fig. 2](image2.png)  
**Fig. 2.** The thermoelectric power $S$ vs. temperature $T$ for single crystals with $y = 0.11$, 0.16, and 0.20 of the $\text{Zn}_x\text{Sb}_y\text{Cr}_z\text{Se}_4$ spinel system.

The magnetic results depicted in Figs. 3 and 4 and in Table II show the strong long-range antiferromagnetic and short-range ferromagnetic interactions evidenced by a shift of $T_N$ to lower temperatures and a susceptibility peak at $T_m$ in the paramagnetic region — to higher temperatures as a magnetic field increases, respectively. The $\chi_{\ac}(H)$ dependence reveals two peaks below $T_N$. First at the critical field $H_{c1}$, connected with a metamagnetic transition and the breakdown of the helical spin structure [2, 3], which slightly decreases with temperature. Second at the critical field $H_{c2}$, connected with the breakdown of the conical spin structure [3], which drops strongly...
Critical fields $H_{c1}$ and $H_{c2}$ at 4.3, 8, 12, 18, 21.2 and 22.8 K of the Zn$_x$Sb$_y$Cr$_z$Se$_4$ single crystals for $y = 0.11$, 0.16 and 0.20.

<table>
<thead>
<tr>
<th>Critical fields</th>
<th>Sb content</th>
<th>$T = 4.3$ K</th>
<th>$T = 8$ K</th>
<th>$T = 12$ K</th>
<th>$T = 18$ K</th>
<th>$T = 21.2$ K</th>
<th>$T = 22.8$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{c1}$ [kOe]</td>
<td>12</td>
<td>13</td>
<td>12</td>
<td>12.5</td>
<td>11</td>
<td>11.5</td>
<td>7.5</td>
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<td>$H_{c2}$ [kOe]</td>
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<td>57.5</td>
<td>55</td>
<td>50</td>
<td>40</td>
<td>40</td>
<td>25</td>
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References

