Spin-driven critical fields in a spinel series based on the matrix ZnCr$_2$Se$_4$

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Abstract. Influence of temperature and magnetic field on critical fields in the frustrated antiferromagnet and semiconductor ZnCr$_2$Se$_4$ doped with Ga, In and Ce is considered. The first critical field, $H_{c1}$, connected with metamagnetic transition remains unchanged with temperature while the second critical field, $H_{c2}$, corresponding to the break-down of the helical spin arrangement drops rapidly with temperature. The sharpness of the $H_{c1}$ and $H_{c2}$ peaks is reduced when the content of the non-magnetic Ga$^{3+}$ and In$^{3+}$ ions in the octahedral positions increases. This phenomenon seems to be connected with the elongation of the interatomic distances leading to the occurrence of the low spin state of the Cr$^{3+}$ ions in the $t_{2g}$ orbital.

1. Introduction

It is well known in literature that ZnCr$_2$Se$_4$ spinel is the matrix of various diluted systems where effects of site disorder, lattice frustration and random distribution of spin interactions create the novel potential applications in spin-based electronic technology. ZnCr$_2$Se$_4$ reveals the spectacular transition to the antiferromagnetic (AFM) state at a Néel temperature $T_N = 20$ K with the dominating ferromagnetic (FM) interactions evidenced by a large positive Curie-Weiss constant $\theta_{CW} = 115$ K [1,2] and accompanied by a 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 structural investigations using synchrotron radiation defined this latter symmetry as orthorhombic $Fddd$ [4]. Previous neutron-diffraction investigations [1,2] of the ZnCr$_2$Se$_4$ spinel showed a spiral AFM spin structure below ordering temperature having a FM arrangement in the (001) planes with a turning angle of 42$^\circ$ between the spins in adjacent (001) planes. A detailed investigation of ZnCr$_2$Se$_4$ single crystal [5] showed the sharp first-order anomalies in the specific heat and negative thermal expansion (NTE) strongly suppressed by external magnetic fields at $T_N$ suggesting a spin-driven origin of the structural transition. They also revealed a metamagnetic transition at the critical field $H_{c1}$ of about 10 kOe for $T = 2$ K, the breakdown of the helical spin arrangement at the critical field $H_{c2}$ of about 65 kOe for $T = 2$ K, and the full saturation magnetisation of about 3$\mu_B$ per Cr ion above $H_{c2}$ for the FM state. At a temperature smaller than
$T_N$, the zero-field-cooling and field-cooling susceptibilities start diverging suggesting a spin frustration [5]. The magnetic isotherm at 4.3 K for a polycrystalline ZnCr$_2$Se$_4$ is shown in Fig. 1. The complex ac dynamic magnetic susceptibility used to study the influence of temperature on critical fields in a polycrystalline ZnCr$_2$Se$_4$ spinel [6] showed a parallel spin coupling in FM clusters in the range between $T_N = 20.7$ K and $\theta_{CW} = 55.1$ K as well as the strong drop of the value of the second critical field $H_{c2}$ with temperature suggesting a spin frustration of the re-entrant type (Fig. 2).

The magnetic and electrical studies carried out on the Zn$_{1-x}$Ga$_{2x/3}$Cr$_2$Se$_4$ poly- and single crystals in the compositional range $0.0 \leq x \leq 0.5$ showed an AFM order below the Néel temperature ($22$ K $\geq T_N \geq 12$ K [7-9]) and the thermally activated $p$-type conduction [8-11]. With increasing Ga content a decrease of $T_N$ [7,8], Curie-Weiss temperature ($118$ K $\geq \theta_{CW} \geq 62$ [7-9]) and effective magnetic moment, ($5.49 \mu_B \geq \mu_{eff} \geq 5.27 \mu_B$ [7-9]) as well as a disappearance of the critical fields [12] were observed.

The magnetic and electrical measurements carried out on the ZnCr$_{2-x}$In$_x$Se$_4$ single crystals in the compositional range $0.0 \leq x \leq 0.14$ revealed an AFM order with metamagnetic phase transitions below the Néel temperature ($22$ K $\geq T_N \geq 16$ K [13,14]) and the thermally activated $p$-type conduction [15,16] for $x \leq 0.07$. With increasing In content a decrease of $T_N$ was observed while $\theta_{CW}$ ($\sim 49$ K), $\mu_{eff}$ ($\sim 5.30 \mu_B$) and the critical fields remained almost constant [14].

The present contribution reports the magnetic properties for ZnCr$_2$Se$_4$ doped with the nonmagnetic Ga and In ions as well as the magnetic Ce ions for which the ion coordination changes from mixed for Ga and In to tetrahedral one for Ce. It seems natural to expect a correlation between the spin state and the critical fields in the disturbed magnetic system. For this purpose the magnetization and the ac dynamic magnetic susceptibility measurements were employed.
2. Experimental

Starting materials for single crystal growth of $\text{Zn}_x\text{Cr}_y\text{Me}_z\text{Se}_4$ ($\text{Me} = \text{Ga}, \text{In}, \text{Ce}$) samples were the binary selenides ZnSe, Ga$_2$Se$_3$, In$_2$Se$_3$ and elementary cerium and selenium. Single crystals were obtained by chemical vapour transport reaction using anhydrous chromium chloride as transporting agent. The chemical composition of the Zn$_x$Cr$_y$Me$_z$Se$_4$ single crystals was analyzed by energy-dispersive X-ray fluorescence spectrometry (EDXRF). The samples were excited using the air-cooled side-window and the Rh-target of the X-ray tube, which allowed a ca. 100 µm nominal focal spot size (XTF 5011/75, Oxford Instruments, USA). A single-crystal X-ray data collection was performed on a Kuma KM4CCD diffractometer with CCD data collector using Mo Kα radiation. The CrystAlis software version 1.170.32 [17] was used for data processing. An empirical absorption correction was applied with the aid of spherical harmonics implemented using a scale 3 Abspack scaling algorithm. The structure was refined by the full-matrix least-squares method by means of SHELX-97 program package [18]. The chemical composition and some data of the crystal structure refinement of the single crystals under study are collected in Table 1. More details are described elsewhere [19].

Table 1. Chemical composition and crystal structure refinement of single crystals under study. The brackets () and [ ] mean tetrahedral and octahedral sites in the spinel structure, respectively. $a$ is the lattice parameter, Cr/Ga-Se, Cr/In-Se and Cr-Se are the interatomic distances in the octahedral sites and Zn/Ga-Se, Zn/In-Se and Zn/Ce-Se are the interatomic distances in the tetrahedral sites [19].

| Composition and refinement | $a$ (pm) | Cr/Ga-Se Zn/Ga-Se (pm) | Cr/In-Se Zn/In-Se (pm) | Cr-Se Zn/Se-Ce-Se (pm) |
|---------------------------|----------|------------------------|------------------------|------------------------|
| (Zn$_{0.98}$Ga$_{0.01}$)[Cr$_{1.92}$Ga$_{0.06}$]Se$_4$ | 1049.71(2) | 6x253.01(2)            | -                      | -                      |
|                           |          | 4x244.25(4)            |                        |                        |
| (Zn$_{0.84}$In$_{0.1}$)[Cr$_{1.78}$In$_{0.14}$]Se$_4$ | 1050.93(3) | -                      | 6x253.22(7)            | -                      |
|                           |          |                        |                        | 4x244.67(4)            |
| (Zn$_{0.86}$Ce$_{0.08}$)[Cr$_2$]Se$_4$ | 1049.37(2) | -                      | -                      | 6x252.83(2)            |
|                           |          |                        | -                      | 4x244.34(4)            |

The magnetization, $\sigma(\mu_0 H)$, and the ac magnetic susceptibility, $\chi_{ac}(T)$, were measured using:
1) a vibrating sample magnetometer with a step motor [20] in the temperature range 4.2–80 K and in applied magnetic induction up to 14 T and 2) a Lake Shore 7225 ac susceptometer in the temperature range 4.2–22 K and in applied external magnetic fields up to 60 kOe, respectively.

3. Results and discussion

3.1. Crystal structure and cation distribution

ZnCr$_2$Se$_4$ crystallizes in a regular system in a spinel type structure and the space group symmetry $Fd\overline{3}m$ (No. 227). In a normal spinel structure Zn$^{2+}$ ions are located at 8$a$ (1/8, 1/8, 1/8) (A site) with tetrahedral environment whereas the Cr$^{3+}$ ions, that are known for a strong octahedral site preference [21], occupy octahedrally coordinated position 16$d$: (½, ½, ½) (B site). Se$^{2-}$ ions are located at the 32$e$ Wyckoff positions. The incorporation of Ga$^{3+}$, In$^{3+}$ or Ce$^{3+}$ into the ZnCr$_2$Se$_4$ does not change the crystal symmetry. Ga$^{3+}$, In$^{3+}$ as well as Ce$^{3+}$ replacement for Zn$^{2+}$ in tetrahedral sites may introduce an increase of the overall positive charge in the crystal that has to be compensated. For first two dopants the compensation comes from cation vacancies that appear at both $A$ and $B$ sites. In (Zn$_{0.84}$In$_{0.1}$)[Cr$_{1.78}$In$_{0.14}$]Se$_4$ there are ~4.6% cation vacant sites whereas in (Zn$_{0.98}$Ga$_{0.01}$)[Cr$_{1.92}$Ga$_{0.06}$]Se$_4$ there are ~1%. In (Zn$_{0.86}$Ce$_{0.08}$)[Cr$_2$]Se$_4$ 2% of vacancies are observed.
only on A site [19]. The lattice parameters and interatomic distances for all compounds are given in Table 1.

3.2. Magnetic properties

The result of measurements of magnetization, \( \sigma(\mu_0 H) \), and ac magnetic susceptibility, \( \chi''(H) \), are presented in Figs. 3-5 and Figs. 7-9, respectively, in order to \((\text{Zn}_{0.98}\text{Ga}_{0.01})\text{[Cr}_{1.92}\text{Ga}_{0.06}]\text{Se}_4\) (a), \((\text{Zn}_{0.84}\text{In}_{0.1})\text{[Cr}_{1.78}\text{In}_{0.14}]\text{Se}_4\) (b) and \((\text{Zn}_{0.86}\text{Ce}_{0.08})\text{[Cr}_{2}\text{Se}_4\) (c). All the magnetic isotherms are similar (Figs. 3-5) and they are comparable to the matrix (Fig. 1) indicating a complex magnetic structure changing from spiral via helical to ferromagnetic one as magnetic field increases. With
increasing temperature a saturation state disappears on going towards the paramagnetic (PM) limit. All the compounds differ in the value of the magnetic moment. When increasing the content of non-magnetic ions in octahedral position of the magnetic moment value is rapidly declining in comparison to the value of 6 $\mu_B$ per molecule for the ZnCr$_2$Se$_4$ matrix at 4.2 K. We have 4.56 $\mu_B$/f.u. for (Zn$_{0.98}$Ga$_{0.02}$)[Cr$_{1.92}$Ga$_{0.06}$]Se$_4$ and 1.06 $\mu_B$/f.u. for (Zn$_{0.84}$In$_{0.16}$)[Cr$_{1.78}$In$_{0.14}$]Se$_4$ in the saturation state. Only for (Zn$_{0.86}$Ce$_{0.04}$)[Cr$_2$]Se$_4$ the saturation magnetic moment reaches the value of 5.89 $\mu_B$/f.u. at 4.2 K which is close to the matrix one. It is known in literature that when only Cr ions occupy octahedral positions in the spinel structure, then they are in the high spin (HS) state with the total spin $S = 3/2$ in the $t_{2g}$ orbital giving the full saturation of about 6 $\mu_B$/f.u. [5].

In order to explain the dramatic undervaluation of the magnetic moment, especially for (Zn$_{0.84}$In$_{0.16}$)[Cr$_{1.78}$In$_{0.14}$]Se$_4$, consider the low spin (LS) state of the Cr$^{3+}$ ions in the $t_{2g}$ orbital. This state seems be connected with a larger lattice parameter of the unit cell entailing the elongation of the interatomic distances observed for (Zn$_{0.98}$Ga$_{0.02}$)[Cr$_{1.92}$Ga$_{0.06}$]Se$_4$ and (Zn$_{0.84}$In$_{0.16}$)[Cr$_{1.78}$In$_{0.14}$]Se$_4$ both in the octahedral and tetrahedral positions (see Table 1). This is a consequence of the replacement of the Cr$^{3+}$ ions by the non-magnetic Ga$^{3+}$ and In$^{3+}$ ions which have larger radii (r$_{Ga^{3+}}$ = 62 pm, r$_{In^{3+}}$ = 80 pm [22]) than Cr$^{3+}$ (r$_{Cr^{3+}}$ = 61.5 pm [22]). In addition, the introduction of non-magnetic ions weakens the AFM superexchange interaction between the Cr ions. Schematically, the population of the HS and LS states for the spinels under study is depicted in Fig. 6. It depends on the content of the non-magnetic ion in the octahedral positions.

![Figure 7](image1.png)  
**Figure 7.** Ac magnetic susceptibility, $\chi_{ac}$, vs. static magnetic field $H$ at 4.3, 10, 18.1 and 21.5 K for (Zn$_{0.98}$Ga$_{0.02}$)[Cr$_{1.92}$Ga$_{0.06}$]Se$_4$. Critical fields $H_{c1}$ and $H_{c2}$ are indicated by arrows.

![Figure 8](image2.png)  
**Figure 8.** Ac magnetic susceptibility, $\chi_{ac}$, vs. static magnetic field $H$ at 4.3, 9.8, 15.9 and 18.2 K for (Zn$_{0.84}$In$_{0.16}$)[Cr$_{1.78}$In$_{0.14}$]Se$_4$. Critical fields $H_{c1}$ and $H_{c2}$ are indicated by arrows.

Figures 7-9 show the critical fields for the spinels under study indicated by $H_{c1}$ and $H_{c2}$ on the curves of the ac magnetic susceptibility versus magnetic field, $\chi_{ac}(H)$, for different temperatures. The first critical field, $H_{c1}$, connected with the metamagnetic transition and the breakdown of the magnetic spiral structure [3,5], slightly decreases with temperature while the second critical field, $H_{c2}$, connected with the breakdown of the magnetic helical structure [5,6], drops strongly with temperature. Above $T_N$ both critical fields disappear. Low sensitivity to temperature of $H_{c1}$ well
correlates with the AFM order in the orthorhombic structure. On the other hand, strong sensitivity to temperature of $H_{c2}$ means that FM coupling is weaker than AFM one, although the FM short-range interactions exist far above $T_N$ in the cubic (spinel) structure as the PM Curie-Weiss temperature ($\theta_{CW}$) is positive and several times larger than $T_N$. The $H_{c1}$ and $H_{c2}$ peaks are not sharp for $(\text{Zn}_{0.99}\text{Ga}_{0.01})[\text{Cr}_{1.92}\text{Ga}_{0.08}]\text{Se}_4$ and the $H_{c2}$ peak is totally fuzzy for $(\text{Zn}_{0.84}\text{In}_{0.1})[\text{Cr}_{1.78}\text{In}_{0.14}]\text{Se}_4$. Only for $(\text{Zn}_{0.86}\text{Ce}_{0.08})[\text{Cr}_2]\text{Se}_4$ the sharpness of the $H_{c1}$ and $H_{c2}$ peaks is comparable with the matrix ones. It means that the spin state strongly influences on the sharpness of the metamagnetic transitions connected with the critical fields. In our case the LS state reduces the sharpness of the magnetic phase transitions, and can even quench them, suggesting spin-driven critical fields in the doped ZnCr$_2$Se$_4$ spinels.

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