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### Title

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#### New materials for spintronics: CuCr<sub>2</sub>Se<sub>4</sub>

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One of the leading fields in magnetism nowadays is the research of new spin polarized materials for spintronics applications.  $CuCr_2Se_4$  can be considered one of them being a highly spin-polarized chalcogenide spinel of interest for magneto tunnel junction [1] as its electrical conductivity and magnetic properties can be chemically tuned by substitution of halogen atoms onto the anion site. In this work we present our data on  $CuCr_2Se_4$  single crystals structurally and magnetically characterized as a function of different  $SeCl_4$  doping level.

Both crystal growth and halogen doping have been obtained by means of the chemical vapor transport technique (CVT) and using powdered Cu, Cr, Se and SeCl<sub>4</sub> as starting materials. Electron microprobe measurements of the crystal and powder compositions (Table 1) show that the doping level depends on the SeCl<sub>4</sub> concentration during growth but saturates at relatively low doping.

Single crystal X-ray diffraction measurements show a rhombohedral structure for the chlorine-doped  $CuCr_2Se_{4-x}Cl_x$ single crystals where ordered substitution of chloride onto selenide sites reduces the symmetry compared to the cubic CuCr<sub>2</sub>Se<sub>4</sub> (Fig. 1). The resulting structure has two octahedral Cr environments (shown in blue) and a pseudo-tetrahedral Cu coordination (yellow). Each Cu tetrahedron consists of one bond to a disordered Se/Cl site and three bonds to sites occupied only by selenium. Similarly, one of the Cr environments comprises six selenium-only sites while the other environment includes a pair of sites, trans to one another, which have disordered occupation by selenium and chlorine dopant. These disordered sites are indicated by red spheres in Fig. 1. Bulk magnetic measurements in order to extract the saturation magnetic moment and the Curie temperature  $(T_c)$  as a function of the doping level have been performed respectively by SQUID magnetometry at 10K and vibrating sample magnetometry (Table 1). While the saturation magnetic moment increases with the doping level, the  $T_{\rm C}$  falls off to lower temperatures with higher concentrations of the chlorine dopant. Surface and element sensitive magnetic measurements have been performed by X-ray circular magnetic dichroism (XMCD). While the lineshape of the Cr  $L_{2,3}$  absorption edges (top of Fig. 2) does not change as a function of the different SeCl<sub>4</sub> doping level, the dichroism (bottom of Fig. 2, normalized here to the max intensity of the absorption at the  $L_3$  edge) shows an increasing magnitude as the doping level increases, in agreement with the SQUID bulk measurements. A smaller dichroism signal (Fig. 3) has also been detected for the Cu at the L<sub>2.3</sub> edges in agreement with previous results [1]. The small induced moment on the Cu is aligned antiparallel to the Cr moment and also increases in magnitude with doping level. Halogen doped CuCr<sub>2</sub>Se<sub>4</sub> single crystals have been also grown with other transport agents (CrCl<sub>3</sub> and SeBr<sub>4</sub>). XAS and XMCD measurements show comparable lineshapes to crystals grown by SeCl<sub>4</sub>.

In conclusion we have synthesized a new structural variation of  $CuCr_2Se_4$  by using the SeCl<sub>4</sub> transport agent. Both bulk and surface magnetic measurements are in agreement in measuring an enhancement in the saturation moment as the doping level is increased. On the other hand, a decrease in  $T_C$  is observed for increasing Cl doping.

SeCl <sub>4</sub> (mg cm <sup>-3</sup> )	Doping level (x)	<b>Τ<sub>C</sub></b> (° <b>C</b> )	Saturation moments (µ <sub>B</sub> /f.u.)
0.00	0.00	157 [2]	-
1.30	0.13	147	0.60
2.66	0.29	133	2.90
4.44	0.28	-	2.25

Table 1: Doping level x in  $CuCr_2Se_{4-x}Cl_x$ ,  $T_C$  and saturation moments as a function of  $SeCl_4$  concentration during synthesis and crystal growth.



Fig. 1: Crystal structure of CuCr<sub>2</sub>Se<sub>4-x</sub>Cl<sub>x</sub>.



Fig. 2: XAS and XMCD at the Cr L<sub>2,3</sub> edges for different chlorine-doped CuCr<sub>2</sub>Se<sub>4-x</sub>Cl<sub>x</sub> single crystals.



Fig. 3: XMCD at the Cu  $L_{2,3}$  edges for different chlorine-doped CuCr<sub>2</sub>Se<sub>4-x</sub>Cl<sub>x</sub> single crystals.

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[2] K. Miyatani, K. Minematsu, Y. Wada, *et al.* J. Phys. Chem. Solids. **32**, 1429 (1971).