

## INFLUENCE OF NICKEL DOPING ON PHYSICAL PROPERTIES OF $\text{ZnCr}_2\text{Se}_4$

**P. Zajdel**<sup>1\*</sup>, **I. Jendrzewska**<sup>2</sup>, **J. Gorau**<sup>1</sup>, **H. Duda**<sup>1</sup>, **T. Goryczka**<sup>3</sup>, and **A. Kita**<sup>2</sup>

<sup>1</sup> *Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland*

<sup>2</sup> *Institute of Chemistry, University of Silesia, ul. Szkolna 9, 40-006 Katowice, Poland*

<sup>3</sup> *Institute of Chemistry and Physics of Metals, University of Silesia, ul. Bankowa 12, 40-006 Katowice, Poland*

Keywords: nickel, spinel, XAS

\*) e-mail: pawel.zajdel@us.edu.pl

$\text{ZnCr}_2\text{Se}_4$  crystallises in spinel structure (SG 227,  $a = 10.48 \text{ \AA}$ ). At 21 K, it orders magnetically into incommensurate helix with propagation vector  $k = (0,0,0.41)$  with a slight tetragonal distortion ( $c/a = 0.9995$ ).

The development of the incommensurate structure is driven by a bond frustration induced by the competition of a nearest neighbour (NN) ferromagnetic superexchange (close to  $90^\circ$  Cr-Se-Cr angle) and numerous NNN antiferromagnetic (AF) interactions. The balance between these interactions can be tuned by doping the system, which may lead to many useful magnetic and electric properties like a spin glass or increased Seebeck effect [1]. But so far, there has been no adequate study of a local structure around the dopant.

We have performed XANES and EXAFS studies of  $\text{ZnCr}_{2-x}\text{Ni}_x\text{Se}_4$  in order to elucidate the influence of Ni on the structural and electronic properties of the system. By the comparison with the Ni K and Cr K edges of monoclinic  $(\text{NiCr}_2)\text{Se}_4$  and the local structure fits using IFFEFIT package, we have confirmed that the Ni is indeed located on the Cr site, since it is not unusual to observe Ni on tetrahedral one [2]. This is also in agreement with the decrease of the lattice parameters due to smaller radius of nickel.

The remaining problem is the nominal oxidation state of nickel. The analysis of the XANES region of Ni K edge revealed that Ni is incorporated in the structure closer to  $\text{Ni}^{2+}$  rather than  $\text{Ni}^{3+}$  state. (We note that the chemical bond in  $\text{ZnCr}_2\text{Se}_4$  has a strong covalent character, so we cannot strictly speak about the oxidation state in an ionic sense) (Fig. 1).

In order to elucidate this result we have performed FPLO calculations of  $\text{ZnCr}_2\text{Se}_4$  and  $\text{ZnCr}_{1.8}\text{Ni}_{0.2}\text{Se}_4$ . The calculated densities of states (DOS) gave a good agreement with the experimental absorption edges. The main nickel contribution to the band structure of the host have been found to be the 3d states located at the Fermi's level, which are polarised opposite to the chromium 3d band (Fig. 2). This is in agreement with the observed decrease of the magnetic moment per formula with increased Ni content.

### References

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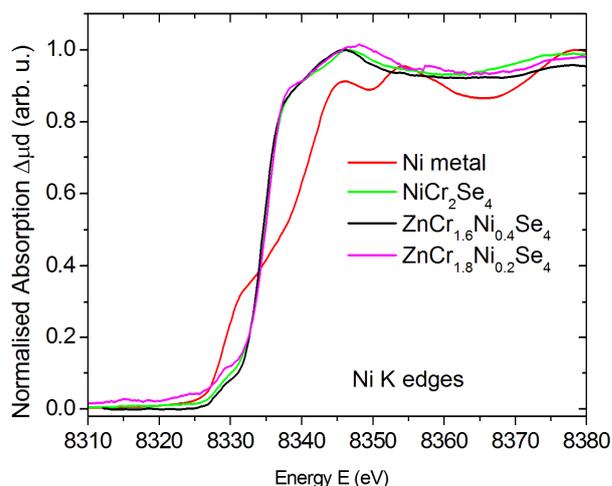


Figure 1. Experimental Ni K absorption edges of  $\text{ZnCr}_{2-x}\text{Ni}_x\text{Se}_4$ , together with standards: Ni-metal,  $\text{NiCr}_2\text{Se}_4$ .

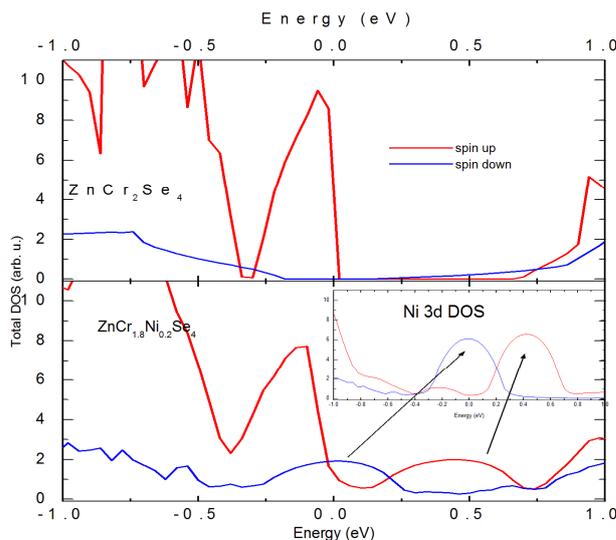


Figure 2. FPLO calculated DOS reveals that Ni 3d levels are situated in the forbidden gap of  $\text{ZnCr}_2\text{Se}_4$  and polarised opposite to chromium.