

Local electronic and crystal structure of CuCr_2Se_4 doped with Ge

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Chromium based chalcogenide spinels (ACr_2X_4 where $\text{A}=\text{Zn}, \text{Cd}, \text{Hg}, \text{Cu}$, $\text{X}=\text{S}, \text{Se}, \text{Te}$) have been researched since 1960's due to their potential applications arising from significant Seebeck coefficient or colossal magnetoresistance [1,2]. Subsequently they were replaced by other compounds but are still promising for further development due to their relative ease of synthesis and great flexibility of the starting matrix.

Current research aims at the enhancement of their response to the magnetic field by increasing bond frustration present in the system through doping of the ferromagnetic metal CuCr_2Se_4 ($T_c = 405 \text{ K}$) with germanium.

In the spinel structure, there are two possible sites for cation doping: tetrahedral (A) and octahedral (trigonal antiprismatic) (B). The nominal compositions of the germanium doped materials $\text{CuCr}_{1.80}\text{Ge}_{0.15}\text{Se}_4$, $\text{CuCr}_{1.80}\text{Ge}_{0.3}\text{Se}_4$ and $\text{CuCr}_{1.90}\text{Ge}_{0.15}\text{Se}_4$ aimed at locating them on the B site. The Ge occupancy refined from XRD was in all cases found to be under 0.15.

Therefore XANES and EXAFS studies were carried out on the CEMO beamline of the DORIS III storage ring in order to elucidate the local electronic and crystal structure around the dopant as well as its influence on the matrix.

The Ge K edges for the germanium doped spinels, presented in Figure 1, are located between spectra for GeSe (nominally Ge^{2+}) and GeSe_2 (Ge^{4+}), which suggests that the formal oxidation state of germanium is forced by the matrix to be close to +3.

Additionally, a systematic shift of edge (see inset in Fig. 1) is observed, indicating that Ge adopts to the charge imbalance caused by the different nominal chromium content.

In order to analyze the electronic structure of the solid solution a DFT based coherent potential approximation (CPA) calculations [3] of a hypothetical $\text{CuCr}_{1.80}\text{Ge}_{0.2}\text{Se}_4$ have been performed and will be compared to the experimental data.

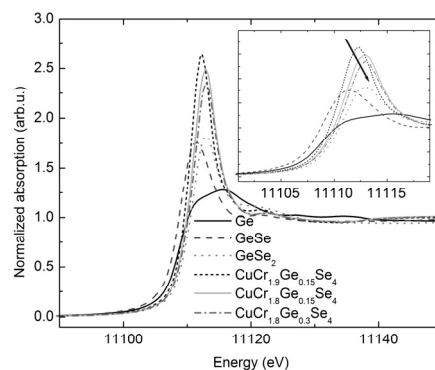


Figure 1. Ge K edges of the studied selenides. Inset shows increasing chemical shift of the Ge K absorption edge from GeSe towards GeSe_2 .

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