ESRF	**Experiment title:** Structure, valence and magnetism of the Zn-Ni-Co-O system	**Experiment number**: HC-2351
Beamline: ID 12	**Date of experiment**: from: 13.7.2016 to: 19.7.2016	**Date of report**: 23.08.2016
Shifts: 18	**Local contact(s)**: A. Rogalev	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

A. Ney*, B. Henne*,V. Ney*, M. de Souza (JKU Linz)

Report:

The aim of the proposal is to study the incorporation of Ni-codopants using x-ray linear dichroism (XLD) and the concomitant modifications of valence and magnetism upon Ni-codoping by measuring x-ray absorption near edge spectroscopy (XANES) and x-ray magnetic circular dichroism (XMCD) in the n-type wurtzite phase (Co:ZnO) and the p-type spinel phase ($ZnCo_2O_4$) of the Zn-Co-O system. During the beamtime range of (Co/Ni)-doped ZnO and Ni-doped $ZnCo_2O_4$ samples grown on sapphire substrates were investigated. In addition, two Ni diffused ZnO single crystals were studied as well. Unfortunately, the quarter-wave plate to switch the linear polarization from horizontal to vertical failed and thus the XLD had to be recorded using circular light under grazing and normal incidence.

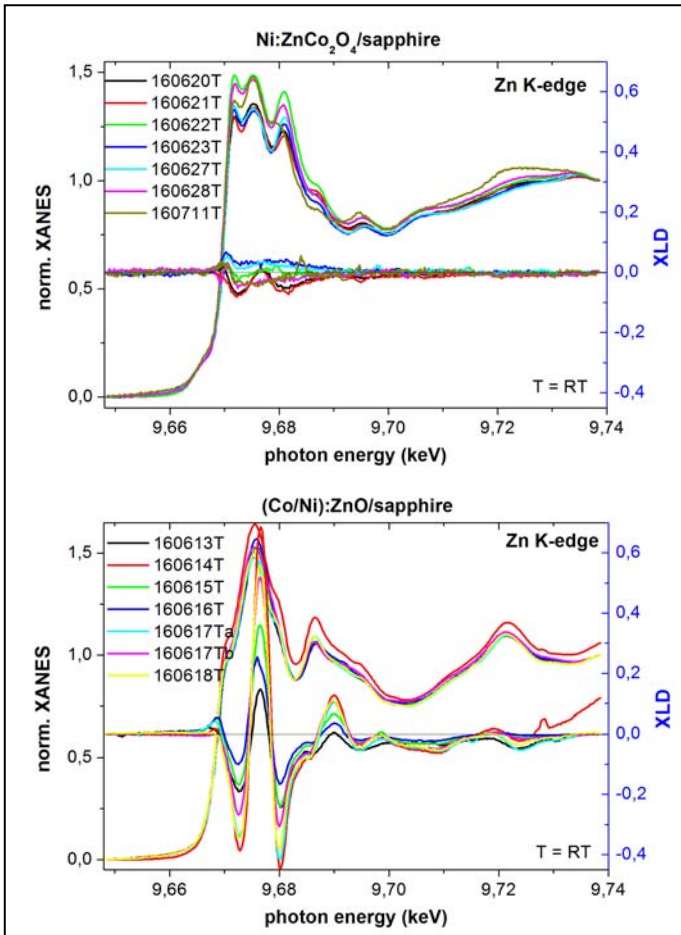

Figure 1: XANES/ XLD at the Zn K-edge for the spinel (top) and the wurtzite (bottom) growth series.

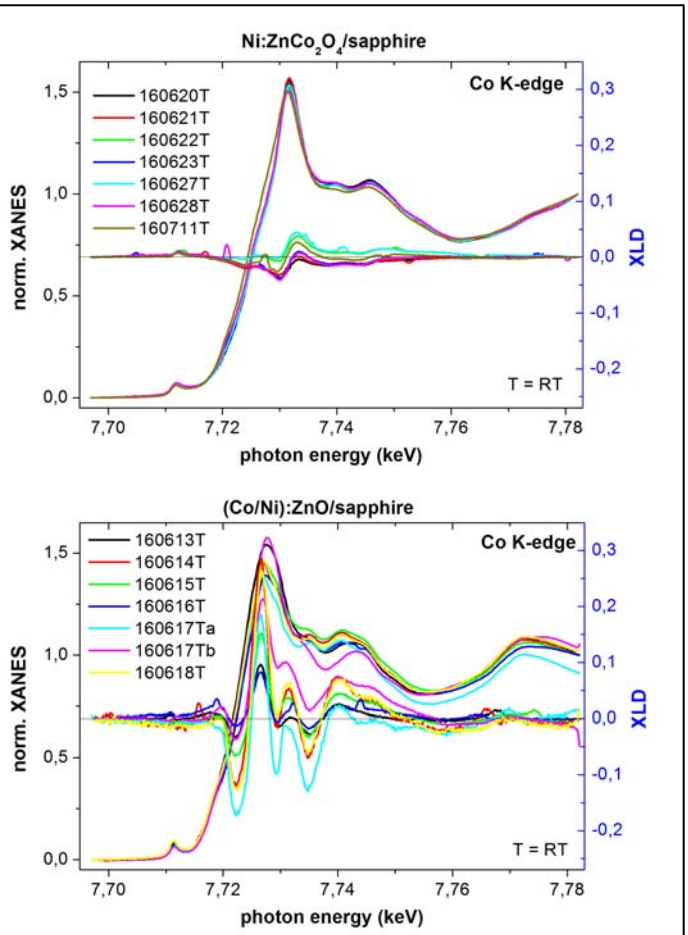

Figure 2: XANES/ XLD at the Co K-edge for the spinel (top) and the wurtzite (bottom) growth series.

This has led to different backgrounds in the respective XANES which reduced the quality and reliability of the resulting XLD spectra. Especially for the samples with low dopant concentrations, in particular the Ni diffused single crystals the resulting XLD spectra were of poor quality. Nevertheless, some conclusions could be drawn from the obtained spectra from the two growth series of wurtzite and spinel respectively. Figure 1 compiles the XANES and associated XLD at the Zn K-edge of the two sample series while Figure 2 shows the Co K-edge and Figure 3 the Ni K-edge. In all three Figures the spinel series in shown in the top panel and the spinel series in the bottom. From the XANES it is visible that while Zn does not change its formal 2+ valence sate in both types of samples, Co exists as 2+ in the wurtzite while it is 3+ in the spinel. Consistently, the XANES and XLD signatures are characteristic for the wurtzite structure while the spinel does not show any significant XLD due to its cubic structure. The most pronounced XLD for the wurtzite series matches with previously introduced quality indicators thus assuring that virtually all Co atoms substitute for Zn. For Ni (Figure 3) the situation is different: while in the wurtzite series hardly any XLD can be observed which indicates that the Ni is not well incorporated into the wurtzite structure but forms a secondary, cubic phase, presumably NiO which is consistent with the fact that no sizable XMCD could be recorded at the Ni K-edge of any wurtzite sample (not shown). In contrast, for the spinel, the XANES is slightly altered compared to the wurtzite samples indicating a slight valence shift for some spinel samples which we tentatively attribute to the fact that Ni can substitute for both Zn and Co, i.e. can be incorporated either on the A or on the B site of the spinel lattice. This has to be confirmed by further simulations using, e.g., the FDMNES code. Finally, we have recorded XMCD spectra and XMCD(H) curves on various spinel samples and one, where SQUID demonstrated ferromagnetic order, is exemplarily shown in Figure 4. A clear XCMD signal can be seen for Co which at low fields follows the SQUID data. At the Ni K-edge the XMCD is less pronounced but the XMCD(H) also follows the SUQID data rather well. Most interestingly, the Ni moments seem to be aligned antiparallel to the Co moments, i.e. this spinel is ferromagnetic.

In summary, we were able to record many XANES, XLD and XMCD spectra for two growth series of the Zn-Ni-Co-O system: the (Co,Ni):ZnO wurtzite and the Ni: $ZnCo_2O_4$ spinel. While Ni – unlike Co – cannot be incorporated into the wurtzite structure of ZnO, in the $ZnCo_2O_4$ spinel Ni in incorporated and its magnetic moments are aligned antiparallel to the Co moments making it a ferromagnetic material.

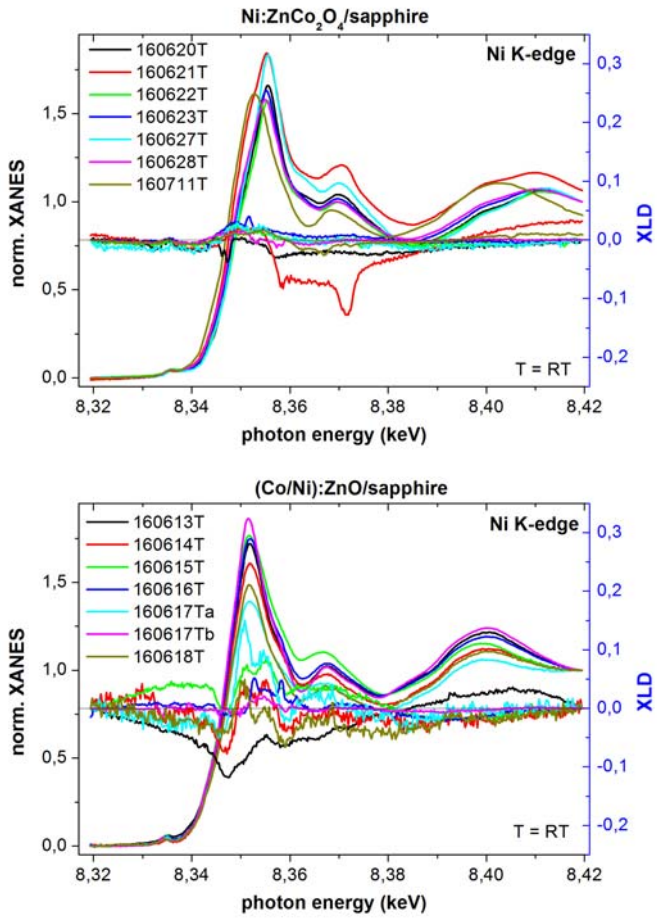

Figure 3: XANES/ XLD at the Ni K-edge for the spinel (top) and the wurtzite (bottom) growth series.

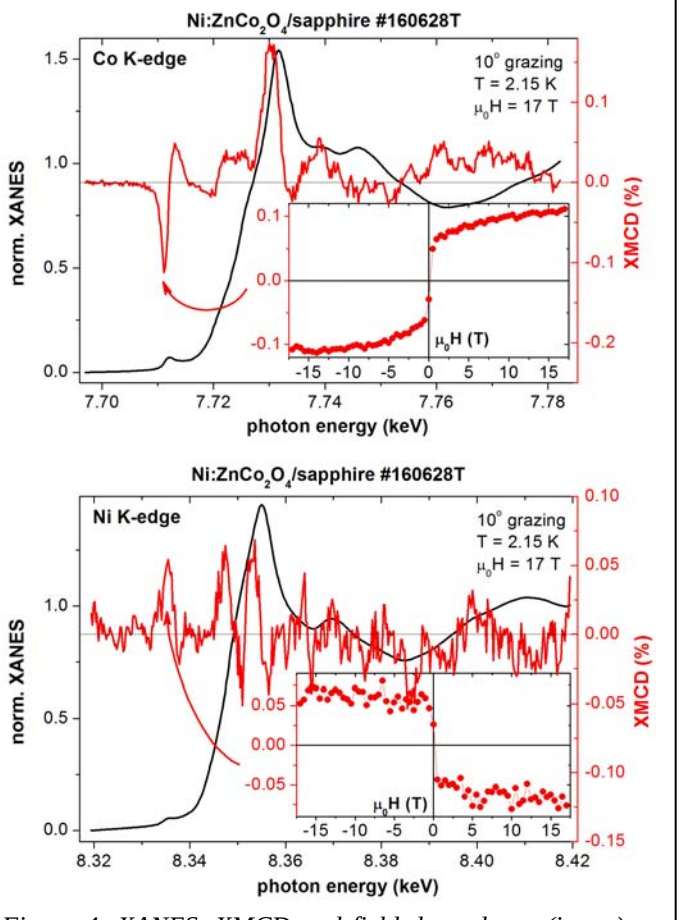

Figure 4: XANES, XMCD and field dependence (insets) at the Co(top) and Ni (bottom) K-edges of the spinel.