ESRF	**Experiment title:** Structure, valence and magnetism of the Zn-Ni-Co-O system	**Experiment number**: HC-2674
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Report:

The aim of the proposal was to continue the previous study (HC-1224) on the structural and magnetic properties of highly Co doped wurtzite ZnO and the spinel $ZnCo_2O_4$, where recent SQUID measurements have revealed a vertical exchange bias effect (vEB) of these uncompensated antiferromagnetic (AFM) oxides. We wanted to compare the vEB measured for the two different local coordination and valence states of the Co (tetrahedral Co^{2+} versus octahedral Co^{3+}). The presence or absence of the vEB shall be confirmed for both species by field-cooled (FC) versus zero-field-cooled (ZFC) experiments at low temperatures and high magnetic fields up to 17 T. During the beamtime range of wurtzite Co-doped ZnO and $ZnCo_2O_4$ spinel samples grown on sapphire substrates were investigated, some of them were also covered with permalloy.

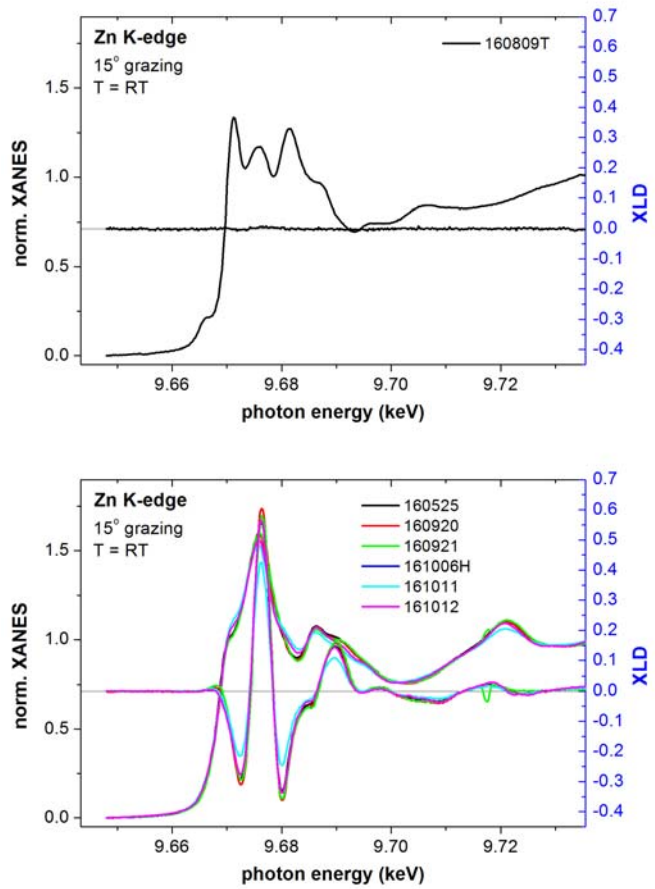

Figure 1: XANES/ XLD at the Zn K-edge for the spinel (top) and the wurtzite (bottom) samples.

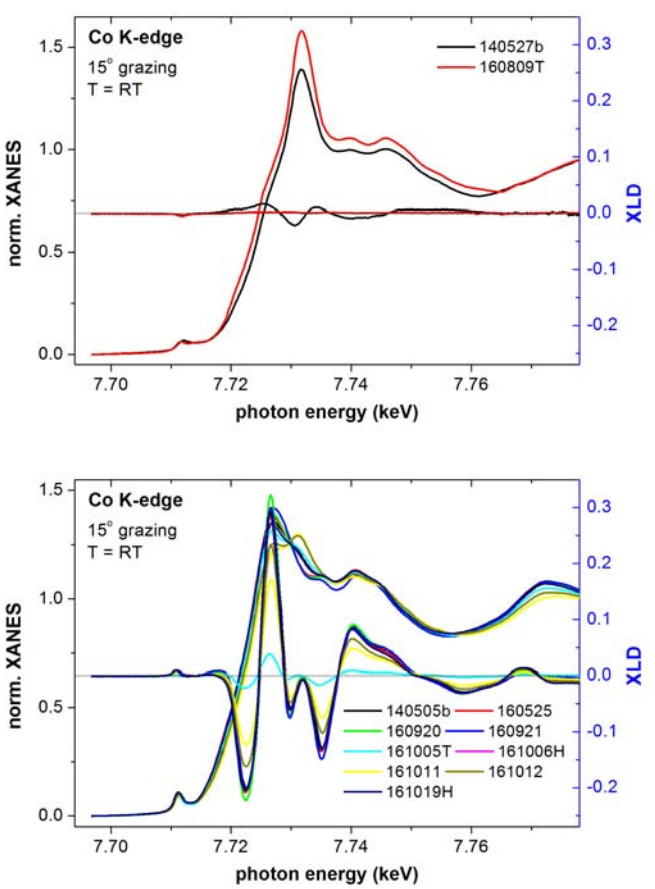

Figure 2: XANES/ XLD at the Co K-edge for the spinel (top) and the wurtzite (bottom) samples.

First of all, one can notice, that in the spinel samples no X-ray linear dichroism (XLD) is measureable at the Zn (Fig. 1, top) and the Co (Fig. 2, top) K-edges, confirming the cubic symmetry of the crystal. The XANES of the Co K-edge furthermore confirms that Co is present in its 3+ oxidation sate while in the wurtzite samples, it is 2+ (Fig. 2). Finally the size of the XLD at both Zn and Co K-edges for the wurtzite samples demonstrates good local crystallinity for most of the samples and these findings were found to be independent from being capped with permalloy or not (not shown).

For a selected set of samples, XMCD spectra have been recorded at 2 K and in external fields of 5T (to be comparable to the SQUID-precharacterization) or 17T after cooling the samples in positive (pFC) or negative (mFC) magnetic fields or in nominally zero field (ZFC). In the course of these measurements two days of experiment were lost, because the persistent switch of the superconducting magnet was initially not connected so that in fact no magnetic field was applied. Interestingly, also at remanence a small XMCD signal could be recorded (not shown). Nonetheless, this finding is not correlated with the original objective of the proposal.

Figure 3 shows p/mFC XMCD spectra for a wurtzite Co:ZnO, which have been cooled in a field of 5T (top) and 17T (bottom). Obviously the signal size at 5T is too small to derive significant conclusions. However, at 17 T (Fig.3, bottom) a clear difference between the p/mFC and ZFC spectra can be seen; interestingly, while the size of the XMCD at the pre-edge feature remains mostly constant, the XMCD at the main absorption increases upon p/mFC cooling and is thus associated with the vertical exchange bias in the system. Note, that this sample was capped with permalloy. Figure 4, top, demonstrates that the behavior does not change when the permalloy is absent and that also for a pure wurtzite Co:ZnO sample the ZFC XMCD at the main edge is smaller than the p/mFC. Figure 4, bottom, in contrast shows a collection of a range of different cooling-experiments for the spinel sample with high A/B disorder. Although a clear vertical exchange bias has been seem in SQUID measurements, the behavior of the XMCD shows no significant differences no matter is cooled in pFC, mFC or ZFC.

In summary, we were able to record a range of XANES, XLD and XMCD spectra for a range of wurtzite and few spines Zn-Co-O samples which demonstrate that cooling-field-associated effects are present in XMCD spectra for wurtzite samples independent of a permalloy cap, while no conclusive results were found in the spinel.

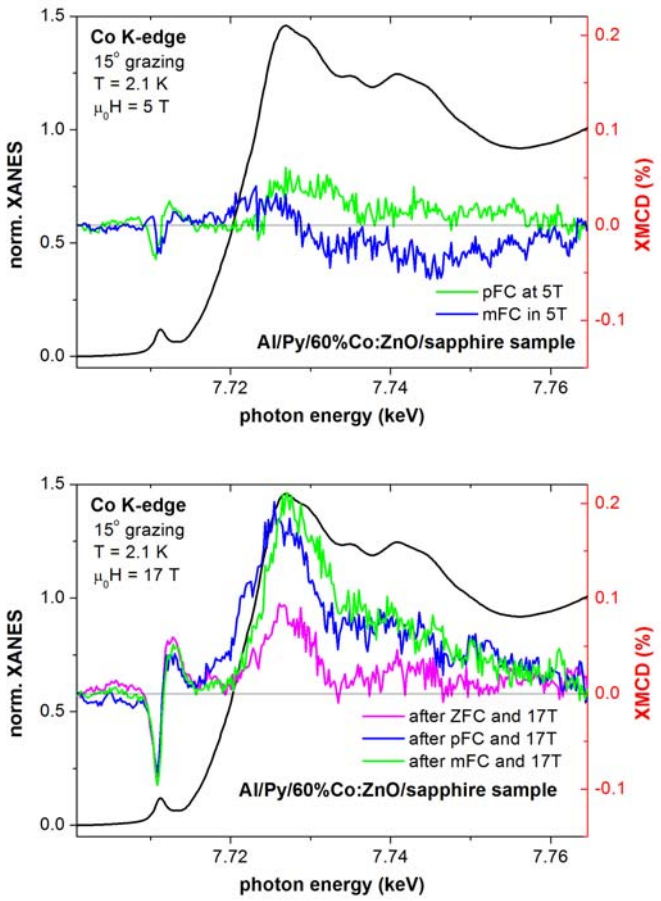

Figure 3: XANES/ XLD at the Ni K-edge for the spinel (top) and the wurtzite (bottom) growth series.

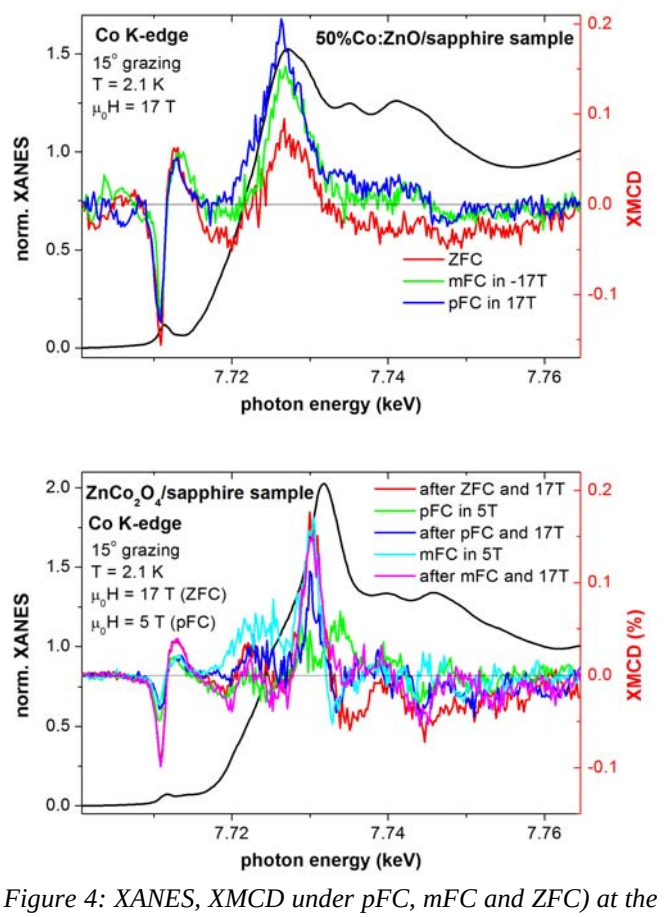

Figure 4: XANES, XMCD under pFC, mFC and ZFC) at the Co K-edges of the bare wurtzite (top) and spinel (bottom).