ESRF	**Experiment title:** Local coordination and magnetism of Co with O: stabilization of CoO in wurtzite structure and the transition to the $ZnCo_2O_4$ spinel	**Experiment number**: HC-1224
Beamline: ID 12	**Date of experiment**: from: 09.07.2014 to: 15.07.2014	**Date of report**: 12.08.2014
Shifts: 18	**Local contact(s)**: F. Wilhelm	*Received at ESRF:*

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Report:

The aim of the proposal is to study the structural and magnetic properties by measuring the x-ray linear dichroism (XLD), the x-ray magnetic circular dichroism (XMCD) of CoO stabilized in the wurtzite phase and the transition to the (cubic) spinel $ZnCo_2O_4$. During the beamtime three different sample series were studied: (i) 30%Co:ZnO films grown from a metallic Co/Zn target using reactive magnetron sputtering with varying oxygen partial pressure from an Ar:O_2 ratio from 10:1 to 10:6 at a substrate temperature of 450°C, (ii) $ZnCo_2O_4$ films grown from a ZnO/Co_3O_4 oxide target grown under varying oxygen partial pressure with an Ar:O_2 ratio from 10:0 to 10:2 at different growth temperatures from 20°C to 525°C, and (iii) $ZnCo_2O_4$ reference films grown by pulsed laser deposition with proven p-type conductivity and thus the Co(III) containing spinel phase. In the following we restrict ourselves to the discussion of the two sample series grown by reactive magnetron sputtering. Figure 1 summarizes all XANES and XLD spectra recorded at the Zn K-edge for sample series (ii) while Figure 2 shows the respective XANES and XLD spectra at the Co K-edge. After a closer inspection of the data the samples can be divided into three sub-categories which are corroborated by lab-based X-ray diffraction (not shown). One sort of samples, typically grown at the highest temperatures shows the typical signatures of the wurtzite (Co:)ZnO samples with a strong characteristic XLD and the associated XANES signatures. The second type is a transition region with suppressed wurtzite XLD signature at both Zn and Co K-edges and a XANES spectrum resembling a mixture between spinel and wurtzite. The third group of samples is virtually pure spinel resembling the reference series (iii) where hardly any XLD is visible. The Zn K-edge XANES is broad and flat without a distinct maximum and the Co K-edge XANES shifts to higher photon energies and develops a strong maximum characteristic for Co(III) (Fig. 2).

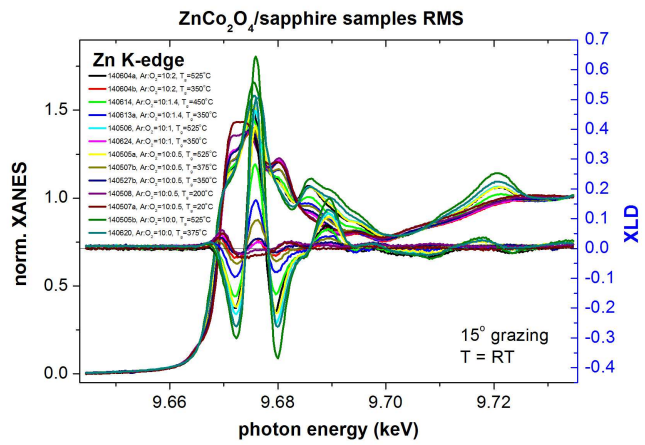

Figure 1: XANES and XLD at the Zn K-edge for all $ZnCo_2O_4$ samples grown from a ZnO/Co_3O_4 target varying oxygen partial pressure as well as growth temperature.

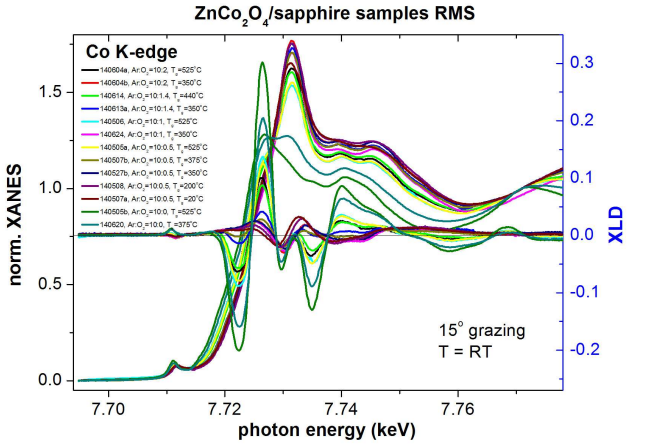

Figure 2: XANES and XLD at the Co K-edge for all $ZnCo_2O_4$ samples grown from a ZnO/Co_3O_4 target varying oxygen partial pressure as well as growth temperature.

We also investigated sample series (i) at the Zn K-edge (not shown) and the Co K-edge (Fig. 3). For a fixed growth temperature one can observe the development of the characteristic spectral features of Co(III) with increasing oxygen partial pressure, especially at an Ar:O_2 ratio of 10:6 (black line). However, this sample is still in the transition regime, where a rather clear wurtzite type XLD is observed, also X-ray diffraction does not detect any spinel reflection. Obviously it is possible to stabilize some fraction of Co(III) in an overall wurtzite type Co:ZnO environment making such samples interesting for more detailed studies with regard to their transport properties. The second interesting observation in Fig. 3 is that it is obviously possible to stabilize ZnO in the pure wurtzite structure even if a third of the Zn cations are replaced by Co, see Fig. 3 blue and cyan lines. This is also corroborated by the Zn K-edge data. Since this is well beyond the coalescence limit of the wurtzite lattice of 20% doping, this sample contains a substantial fraction of CoO in wurtzite structure; we even have measured one sample containing 40% of Co (not shown). Obviously it is possible to stabilize either Co(II) in wurtzite environment or Co(III) either in wurtzite or in spinel environment depending on the chosen preparation conditions irrespective of the use of oxide or metal targets. The tendency is that high growth temperatures and low oxygen partial pressures favor wurtzite and low temperatures and/or high oxygen partial pressures favor spinel type samples. The XANES and XLD data recorded during this experiment lay the foundations to understand the transport and global structural properties on a microscopic scale where a clear interrelation of Co species and physical properties can be made on solid grounds.

We have also studies the magnetic properties of a selected set of samples from series (i) and (ii) with a focus on disentangling the magnetic properties of Co(II) in wurtzite environment, which are well-known from previous experiments on phase pure Co:ZnO samples and could be found here for the 30% and 40% Co:ZnO smape grown with an Ar:O_2 ratio of 10:1 (not shown), and of Co(III) in the spinel environment. Figure 4 summarizes the XMCD spectra of different samples which are representative of the different sub-categories as found by the analysis of the XLD data. We have also recorded the field dependence of the XMCD at various photon energies of the distinct spectral features seen in the XMCD spectra (not shown). While Co(ii) is best measured at the pronounced pre-edge feature, this magnetic signature decreases upon going towards the spinel type Co(III) also, the maximum of the XMCD at the main absorption shifts to higher energies by going from Co(II) towards Co(III) so that one can record valence-selective XMCD(H) curves at these distinct features. However, the high field data suggest, that at both species there seems to be a tendency for antiferromagnetic coupling of the adjacent Co moments, since in all samples a finite slope of the XMCD(H) curves is found which is suggestive of these types of samples being a sort of uncompensated antiferromagnet. Figure 4 also contains one interesting sample, where a strong up/down feature can be seen in the XMCD. At present the origin of this is still unclear but it could be taken as a hint of antiparallel coupling of Co(II) and Co(III) moments which could open perspectives to tailor magnetic properties in A/B disordered spinel samples by this antiparallel alignment of Co moment of different size.

In summary, we have measured a comprehensive set of samples based on the Zn-Co-O system where we could identify distinct spectroscopic features of Co(II) and Co(III) in different structural environments and further identify the characteristic magnetic properties. This large set of spectroscopic data will enable us in to establish reliable relationships between global physical properties and the responsible Co species.

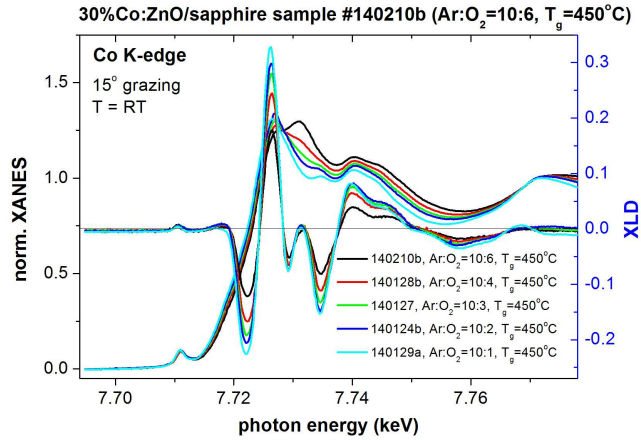

Figure 3: XANES and XLD at the Co K-edge for all 30%Co:ZnO samples grown from a Zn/Co target with varying oxygen partial pressure.

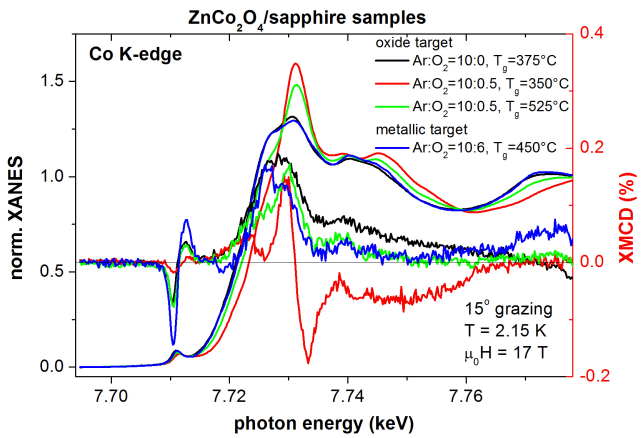

Figure 4: Comparison XANES and XMCD spectra of various Co:ZnO and $ZnCo_2O_4$ films measured at 2K and 17T under grazing incidence.