ESRF	**Experiment title:** Probing the transition from high crystallinity towards amorphization and its interplay with magnetism in double-doped magnetic oxides	**Experiment number**: HE-3902
Beamline: ID12	**Date of experiment**: from: 13.11.2012 to: 20.11.2012	**Date of report**:
Shifts: 18	**Local contact(s)**: Katharina Ollefs	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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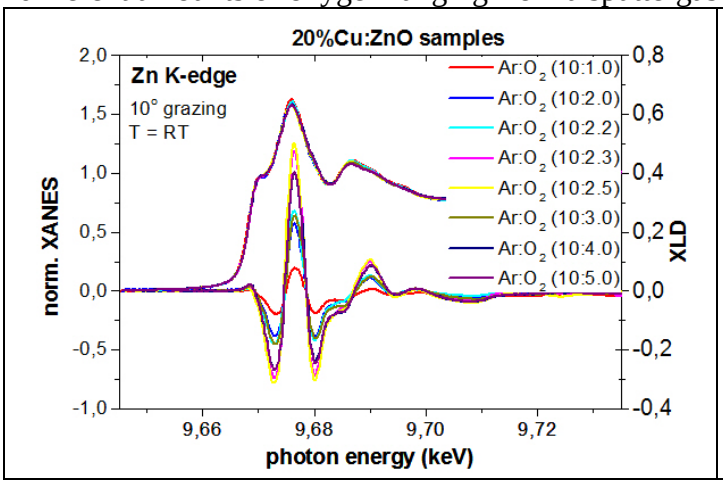
Report:

The aim of this proposal was to investigate the X-ray linear dichroism (XLD) and the X-ray magnetic circular dichroism (XMCD) of doubly doped ZnO films as a function of the Co/Cu dopant concentration. The XANES, XLD and XMCD should have been measured at the K-edges of Co, Cu and Zn, as well as XMCD and element selective M(H) curves at the K-edges of Co and Cu of Co-doped, Cu-doped and Co/Cu co-doped ZnO epitaxial films. Cu:ZnO films with nominally 10% and 20% Cu were measured, as well as CuCoZnO samples with 10% Cu and 10% Co. For the Cu:ZnO and the CuCoZnO films we looked at series with different amounts of oxygen ranging from a sputtergas ratio of Ar:O_2 of (10:1) to (10:5).



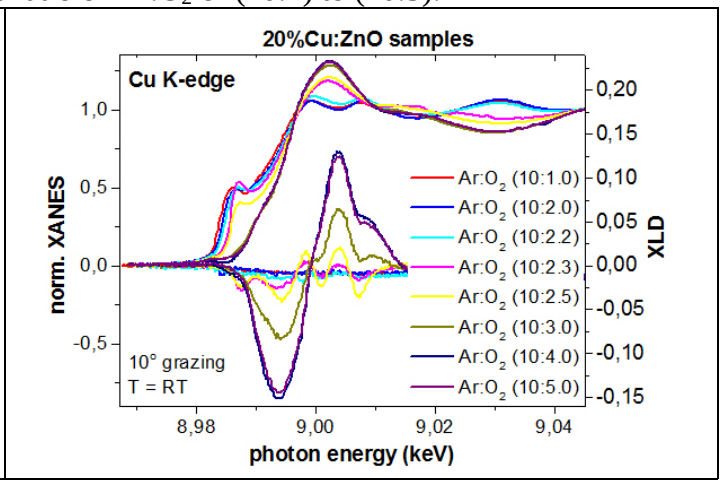
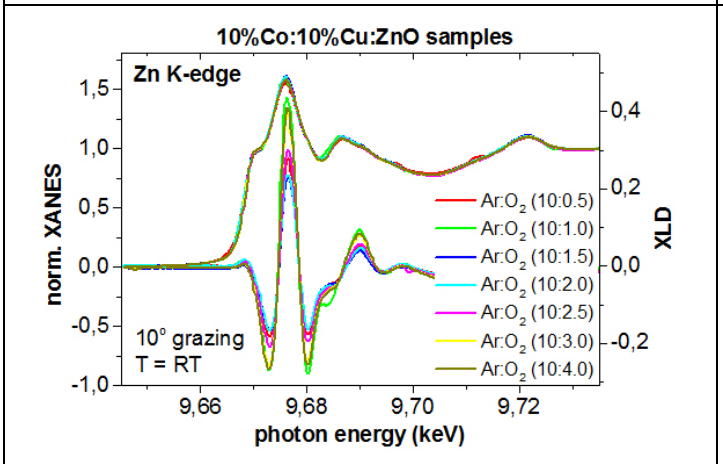


Figure 1 XANES and XLD at the Zn K-edge of 20%Cu:ZnO and 10%Co:10%Cu:ZnO sputtered with different Ar:O_2 ratios.



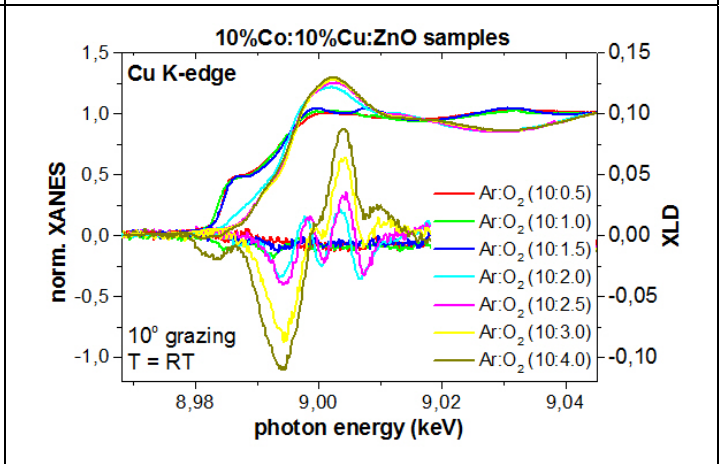


Figure 2 Cu K-edge XANES and XLD of the sputter gas series of 20%Cu:ZnO and 10%Co:10%Cu:ZnO.

For all films we were able to record the XANES and the corresponding XLD at the Zn, Co and Cu K-edges. A different ratio of the sputtergas Ar:O_2 leads to different sizes of the XLD at the Zn K-edge (figure 1) and significant different spectral features at the Cu K-edge (figure 2). For the CoCuZnO samples (figure 1 and 2 bottom) the (10:1) exhibits the largest XLD at the Zn K-edge, which is the same optimum ratio as for Co:ZnO samples (as measured in previous beamtimes (HE-2399, HE-2714 and HE-3292)). However, at this ratio the XLD at the Cu K-edge is negligible small indicating negligible substitutional incorporation of Cu. Also the respective XLD at the Co K-edge is reduced (figure 3). In CuZnO samples the XLD at the Zn K-edge in in general reduced compared to CoZnO (figure 1, top). In summary, the very high solubility of Co in the ZnO wurtzite crystal structure can thus not be reproduced for Cu and Co addition does not improve it.

The XMCD has been measured at the Co and the Cu K-edge for three selected samples respectively. In figure 4 the isotropic XANES and the XMCD of the CuCoZnO samples with an Ar:O_2 ratio of (10:3) and (10:5) are shown at the Co K-edge. In the XANES and in the XMCD the strong difference between these two samples are obvious. The green arrow marks the region, where metallic Co has its mayor XMCD. For the (10:3) sample, no XMCD is measurable there, whereas for the (10:5) sample a clear dichroism can be seen. For both samples a dichroism at around 7.711 keV appears, which is typical for Co^{2+}. This feature is reduced for the (10:5) sample. To distinguish between the Co^{2+} atoms and the metallic Co, XMCD(H) curves were taken at low temperatures (2.15 K) at the Co K-edge (figure 5).

At the Cu K-edge the size of the XMCD was less than 0.1% for the three measured samples: the CuCoZnO samples (10:3) and (10:5), and the 20% Cu:ZnO sample (10:2.3) (not shown) and no characteristic dichroism could be measured (figure 6). The magnetic correlations between the Co and Cu subspecies were supposed to be unraveled with these measurements. Since no XMCD was measurable at the Cu K-edge, the magnetic properties of the samples can solely be assigned to the Co atoms consisten with the low solubility of Cu in ZnO.

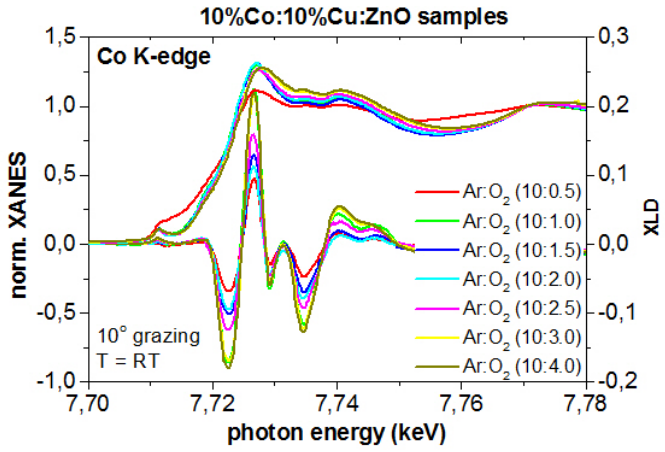


Figure 3 Co K-edge XANES and XLD of CoCuZnO.

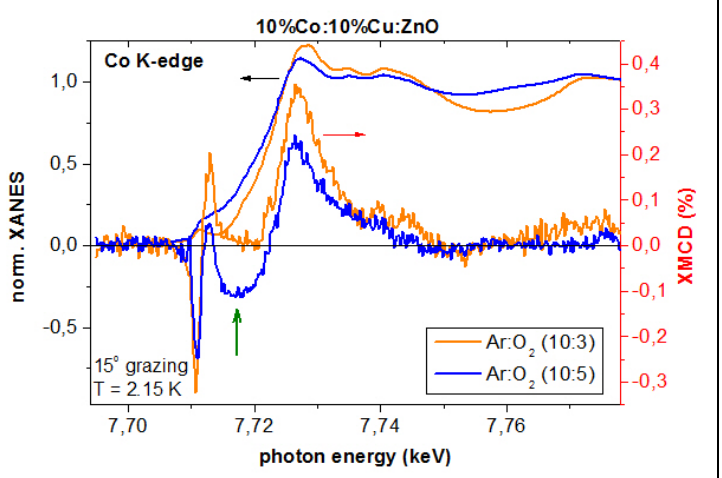


Figure 4 Co K-edge and XMCD of CoCuZnO with an Ar:O_2 ratio of (10:3) and (10:5). The green arrow marks the region of metallic Co.

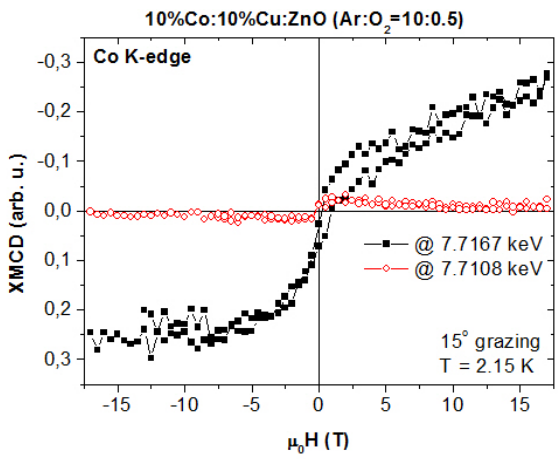


Figure 5 XMCD(H) at 7.7167 keV corresponding to metallic Co and 7.7108 keV to Co^{2+}.

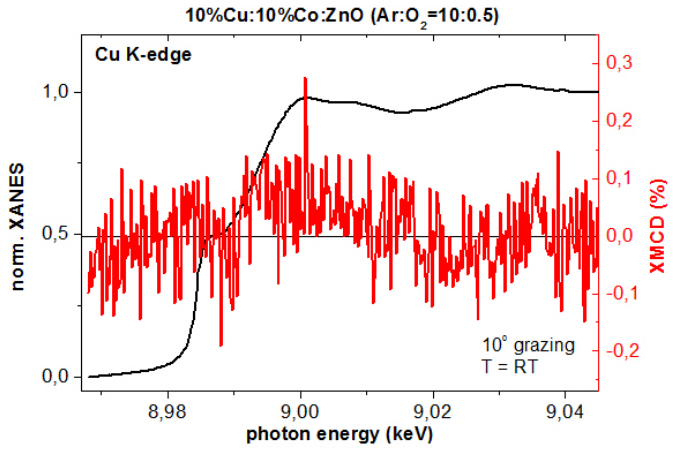


Figure 6 Isotropic XANES and XMCD at the Cu K-edge of CuCoZnO with an Ar:O_2 ratio of (10:5).