ESRF	**Experiment title:** Origin of long range magnetic order of Gd:ZnO probed by XMCD at the Gd L-edges and Zn K-edge	**Experiment number**: HE-2399
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Report:

We measured the x-ray linear dichroism (XLD) at the Zn and the Co K-edge and at the Gd L_3-edge on Gd- and Co-doped ZnO samples grown by pulsed laser deposition (PLD), magnetron sputtering, chemical vapor deposition (CVD) on sapphire and ion implantation of ZnO single crystals. The results for the Zn K-edge are summarized in Fig. 1. Comparing the magnitude of the XLD signal between the different preparation techniques the wurtzite quality increases from CVD over sputtered to PLD grown ZnO films which will be quantified by FDMNES simulations as done before (A. Ney et al., Appl. Phys. Lett. **90** (2007) 252515). The measurements on the ZnO single crystals have to be corrected for self-absorption effects and will serve as reference in the future. On the contrary, SQUID measurements on these samples show increasing ferromagnetic-like signatures from PLD over sputtered to CVD. Further XLD experiments have been performed at the dopant edges of all samples. For the ion-implanted ZnO

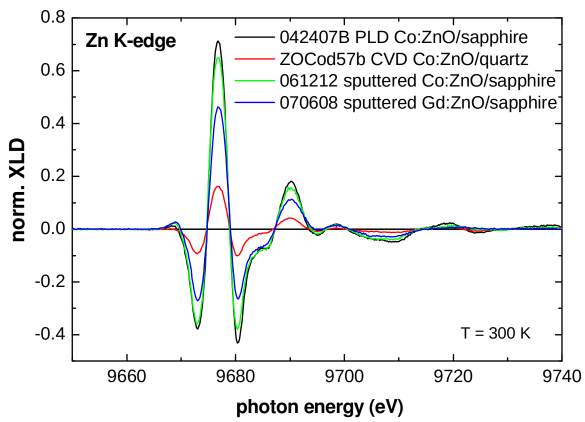

Figure 1: Normalized XLD spectra at the Zn K-edge of Co doped ZnO samples grown by different techniques. The quality of the local wurtzite structure is best for the PLD sample and worst for the CVD grown films. Sputtered Gd and Co doped ZnO is shown as well.

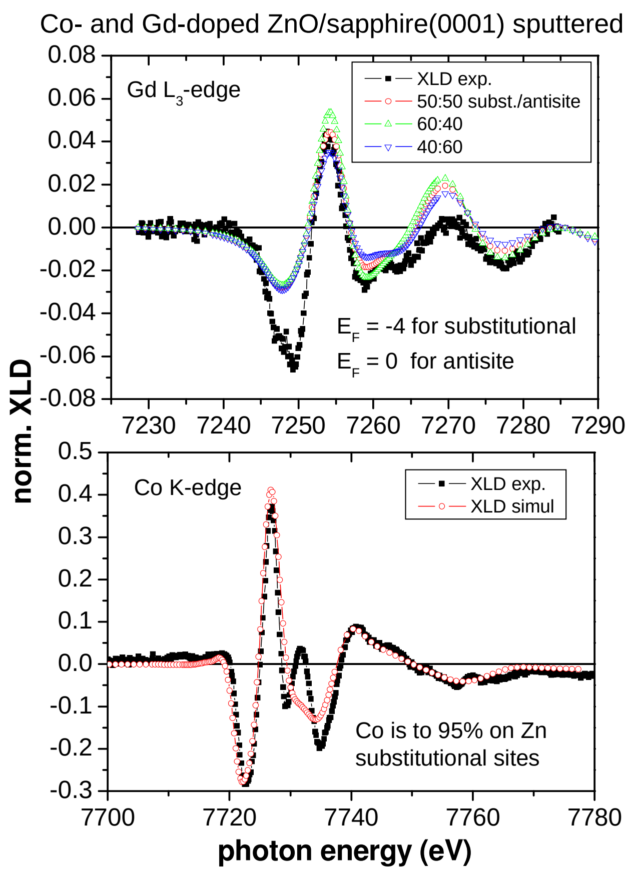

Figure 2: Normalized XLD spectrum at the Gd L3-edge and the Co K-edge of sputtered ZnO films.Whereas for Gd the simulations indicate that substitutional sites are not preferred, 95% of the Co atoms go to Zn substitutional sites as revealed by simulations of the respective XLD spectra.

single crystals the implantation dose was too low to detect any absorption signal, although the area dose of $10^{15}/cm^2$ is close to the amorphization limit. The PLD grown samples exhibit a clear wurtzite signature at the Co K-edge (very similar to the one shown in Fig. 2). Figure 2 shows the comparison between the Gd- and Co-doped sputtered ZnO films together with preliminary simulations. It is obvious that unlike Co the Gd atoms do not prefer Zn substitutional sites in this type of samples.

The magnetic investigations are shown in Figure 3 for the sputtered Gd-doped ZnO sample. A clear dichroic spectrum at the Gd L_3-edge is visible; however, the element specific hysteresis reveals purely paramagnetic behavior. At first sight the lesser structural quality of this sample can be made responsible for the absence of ferromagnetic-like order. On the other hand, comparing this with the highest quality sample – the PLD grown, Zn diffused Co-doped ZnO film – shown in Figure 4, it is obvious, that also here ferromagnetic signatures are absent. Nevertheless, some other interesting observations can be made. First, the pre-edge feature at the Co K-edge clearly demonstrates, that Co is not in a metallic state, but only introducing a defect level with strong magnetic polarization. The element specific hysteresis can be recorded both at the pre-edge feature and at the main peak with opposite sign. The magnetic investigations shown in Figure 4 together with the structural characterization shown in Figure 1 lead us to the conclusion that ferromagnetic-like behavior is absent in high-quality samples as well.

To summarize our findings we can state that in the case of ZnO all four different preparation methods, PLD, CVD, sputtering and ion-implantation, lead to different structural qualities, although information on the dopant location for the implanted sample is still missing. In general, the Co samples show more and more ferromagnetic-like signatures in SQUID experiments when the structural quality decreases. Also antisite disorder creates paramagnetic behavior as can be seen from the Gd doped sample of lesser quality. Thus, the origin of the ferromagnetic-like signatures may be little Co metallic clusters. The occurrence of such clusters can be ruled out for the samples studied here by means of the existence of the pre-peak feature at the Co K-edge. For the Gd L_3-edge no pre-edge feature exists and therefore the existence of metallic clusters can only be ruled out by means of XLD simulations. It would be desirable to further investigate higher implanted samples, since these show ferromagnetic-like signatures by means of SQUID and to study ZnO samples which contain metallic Co clusters to further solidify our results.

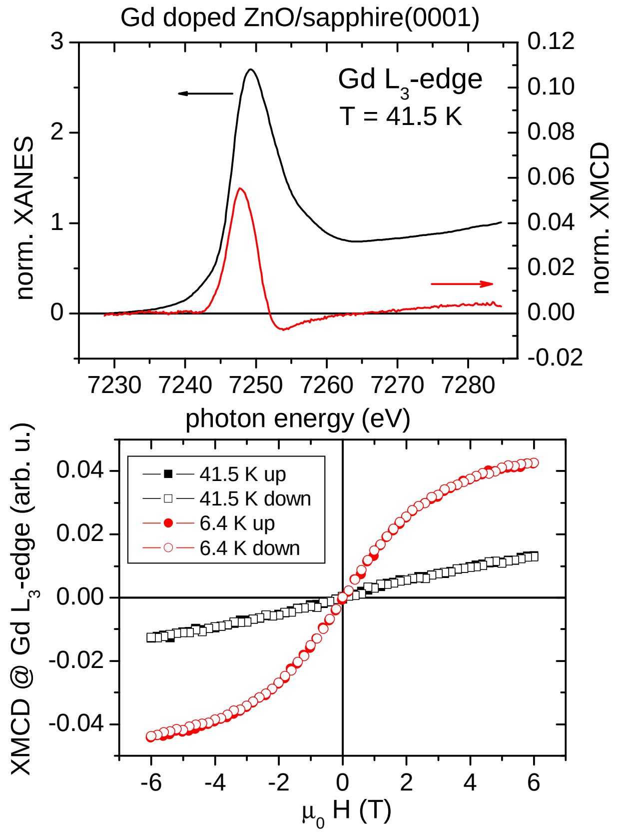

Figure 3: Absorption and XMCD spectra for the sputtered Gd doped ZnO film. The element specific hysteresis demonstrates that the sample exhibits paramagnetic behavior.

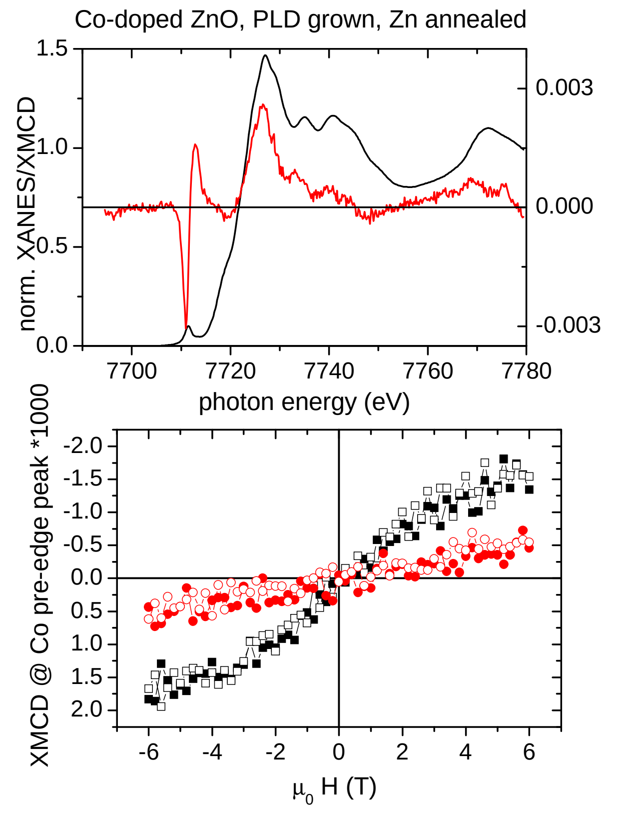

Figure 4: Absorption, XMCD and element specific hysteresis for PLD grown Co:ZnO. Again, only paramagnetic signatures are visible. The pre-edge featurte rules out metallic Co.