ESRF	**Experiment title:** Clarification of the magnetic structure of the beta-phase of MnAs	**Experiment number**: HE-2714
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Report:

The aim of this experiment was to clarify the origin of long range magnetic order of Co and Gd doped ZnO films grown on sapphire. Since all Gd doped samples were paramagnetic by means of SQUID, we had to focus on the Co doped samples. The samples were prepared by reactive magnetron sputtering and ion implantation, respectively. The findings can be compared to earlier experiments using PLD grown samples. (HE-2399 and A. Ney et al. PRL **100** (2008), 157201) Most importantly, we can show, that the best quality

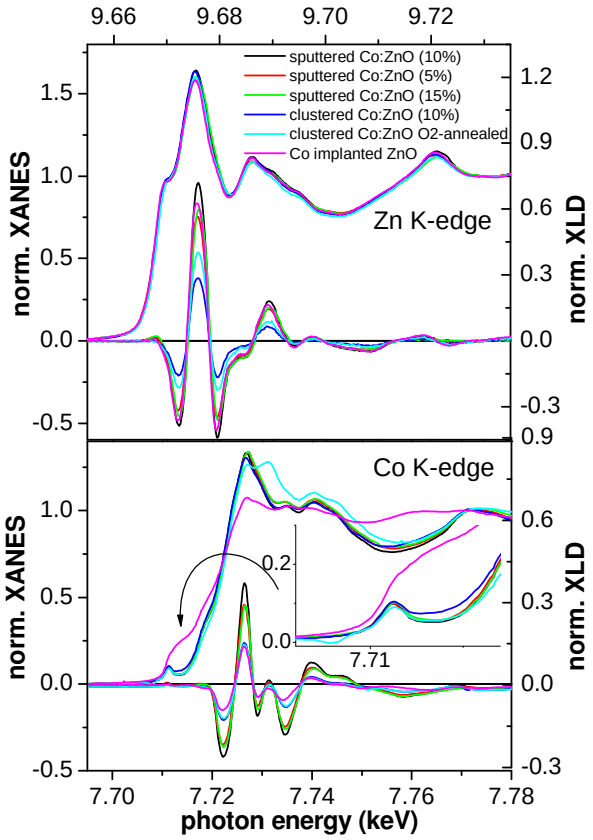

Figure 1: XLD spectra recorded at the Zn and Co K-edge of various Co doped ZnO films grwon on sapphire. 5%, 10% and 15% of Co doping results in comparable structural quality. Co Implantation leads to metallic Co and Oxygen-deficient growth to Co cluster formation which are easily oxidized towards CoO.

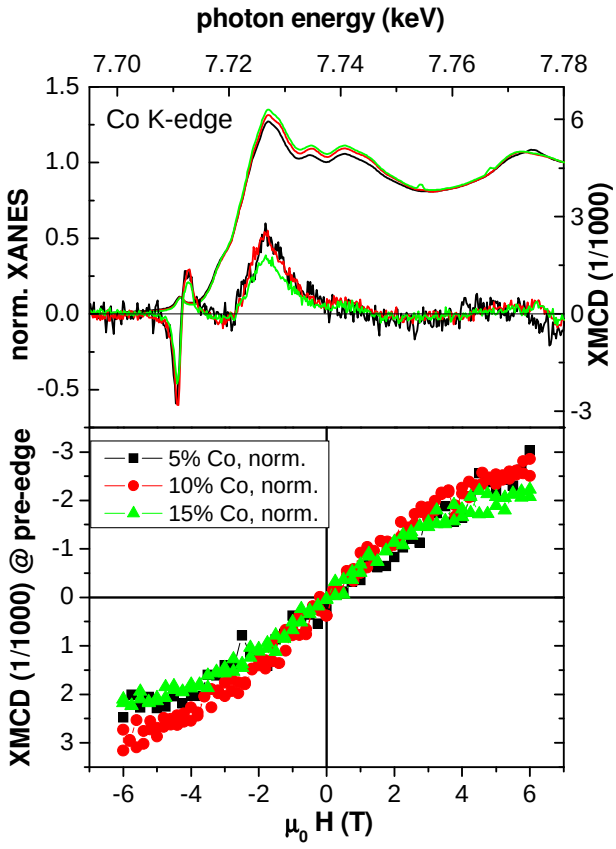

Figure 2: XMCD spectra and element specific hysteresis at the Co K-edge for 5%, 10%, and 15% Co doped ZnO. The XMCD at 15% is slightly reduced both at the pre-edge and at the main peak.

samples prepared by reactive magnetron sputtering containing 5%, 10% and 15% Co, respectively, lead to the same excellent structural properties as probed by XLD, see Fig. 1. The XMCD spectra and M(H) curves in Fig. 2 demonstrate that the Co is in its 2+ oxidation state and the behavior is purely paramagnetic. XMCD of the 15% Co:ZnO sample is slightly reduced, presumably due to the formation of antiferromagnetic Co-O-Co pairs. Figure 1 shows for comparison a 10%Co:ZnO sample which was grown under reduced oxygen partial pressure. This sample shows room-temperature magnetic order by means of SQUID and annealing this sample in oxygen turns this sample paramagnetic again Preliminary XRD and EPR/FMR investigations point towards a Co/CoO-cluster formation. Figure 1 reveals that the Co XLD is reduced as well as the pre-edge feature, but the XANES still resembles Co2+. The size of the XLD does not change upon oxygen annealing but the XANES is strongly altered. Figure 1 also shows a Co ion implanted ZnO sample which has a comparable low XLD and a XANES which is characteristic for metallic Co. The XMCD spectra shown in Fig. 3 compare the Co ion-implanted sample to the clustered Co:ZnO sample. At low temperature a clear pre-edge XMCD is visible which is reduced in size compared to the ones in Fig. 2. The same sample at 250 K shows a very different spectral shape of the XMCD which is quite similar to the one recorded at the Co-implanted sample. We have to conclude that this sample contains a fraction of substitutional Co2+ which is not affected by annealing procedures and which accounts for the XLD signature and some metallic Co forming clusters which accounts for the observed magnetic order at elevated temperatures. Oxygen annealing of this sample leads to paramagnetism as measured with SQUID; however, the element specific M(H) curves on this sample shown in Fig. 4 reveal, that the oxygen annealed clustered Co:ZnO sample is not purely paramagnetic. Fig. 4 contains for comparison a M(H) curve on the best quality 10% Co:ZnO sample shown in Figs 1 + 2. The M(H) curve at 7 K is typical for paramagnetism. We also cross-checked that the main feature shows the same M(H) curve with opposite sign (not shown). The surprising shape of the M(H) curve in Fig. 4 can be deconvoluted using the size of the XLD at the Co edge. The size of the XLD leads to the conclusion that about 40% of the Co are on substitutional Zn sites, which are paramagnetic (and cause the SQUID signal of this sample). If one subtracts this fraction of Co having the same M(H) curve like the best quality sample, one yields the same M(H) curve as measured at the main peak (green triangles). Looking again at the Co XANES, one can do a similar deconvolution resulting in a XANES which is more typical for CoO (not shown). We therefore have to conclud that Co 2+ on Zn substitutional sites only explain paramagnetism in agreement with our earlier findings (PRL **100** (2008) 157201) the magnetic response at elevated temperatures are caused by metallic precipitation and subsequent oxygen annealing leads to CoO-like XANES and the M(H) curves in Fig. 4 which requires further investigations.

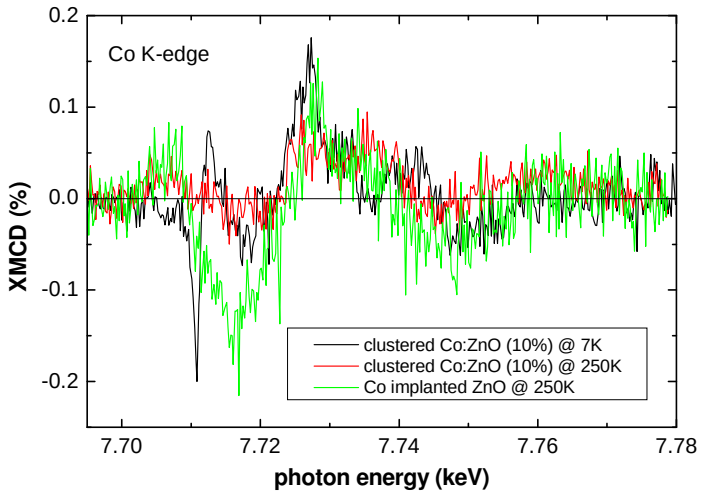

Figure 3: XMCD spectra for the clustered sample at 7K and at 250K; the XMCD at the pre-edge is absent at 250K and very similar to the typical metallic Co XMCD of the implanted sample.

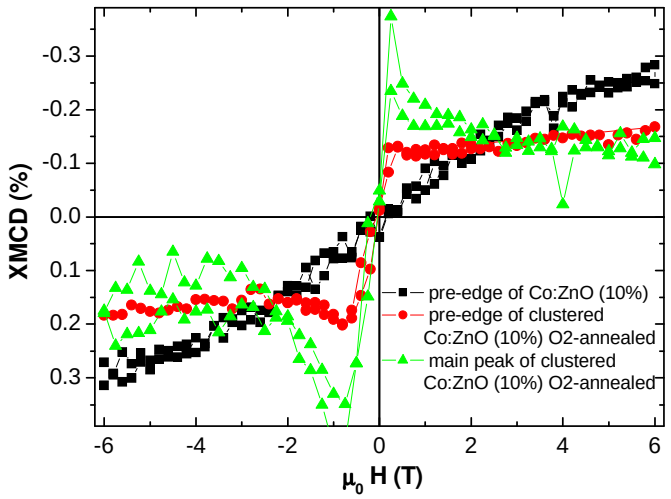

Figure 4:. Element specific hysteresis of the dilute and clustered Co:ZnO sample at the pre-edge and at the main peak; see text.