ESRF	**Experiment title:** Study of the AFM Co-O-Co exchange in Co:ZnO at high magnetic fields	**Experiment number**: HE-3292
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Shifts: 18	**Local contact(s)**: F. Wilhelm	*Received at ESRF:*

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Report:

The aim of this experiment was to study investigate the XMCD and the respective element specific M(H)-curves at high magnetic fields up to 17 T and at low temperatures (2.5 K) of the Co K-edge of paramagnetic (PM) Co:ZnO samples grown on c-sapphire to directly evidence the presence of an antiferromagnetic (AFM) next cation neighbour exchange by the presence of a spin-flop transition for samples with 5%, 10% and 15% of Co doping. In addition, one N-codoped Co:ZnO sample with high structural quality and a superparamagnetic (SPM) Co:ZnO sample with evidenced phase separation were studied.

During the beam time a series of Co:ZnO epitaxial films on c-plane sapphire was studied at the lowest accessible temperature of 2.5 K. For all samples XMCD spectra were recorded at 17 T applying the magnetic field in the film plane (H ⊥ c) reversing both the helicity of the light as well as the magnetic field direction. For two samples (one PM 10% and one PM 15% Co:ZnO film) the spectra were recorded in the out-of-plane geometry as well (H ∥ c). Figure 1 shows the XANES and related XMCD signal recorded at the Co K edge of the PM 10% Co:ZnO film for both orientations. The spectral features of the XMCD are identical to previously recorded XMCD at 6.5 K and 6 T (see e.g. HE-2399) and no obvious discrepancies are visible for the two orientations of the magnetic field. However, a closer inspection reveals that the XMCD at the pre-edge feature (at 7.71 keV) exhibits a slightly smaller amplitude and is narrower in energy for the out-of-plane geometry. The XMCD at the main edge (at 7.725 keV) has a slightly altered shape as well. Similar observations could be made for the 15% Co:ZnO film (not shown). The origin of this discrepancy is not clear so far and XMCD spectra with improved signal-to-noise ratio would be desirable for further analysis. Figure 2 displays the element-specific M(H) curves of the same film recorded at the maximum dichroic signal at the

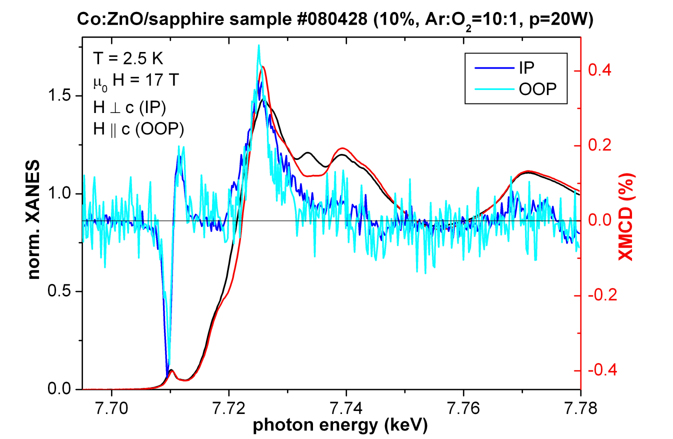

Figure 1: XANES and XMCD spectra at the Co K-edge of 10% Co:ZnO films recorded at 2.5 K and 17 T for two orientations of the magnetic field (in- and out-of- plane).

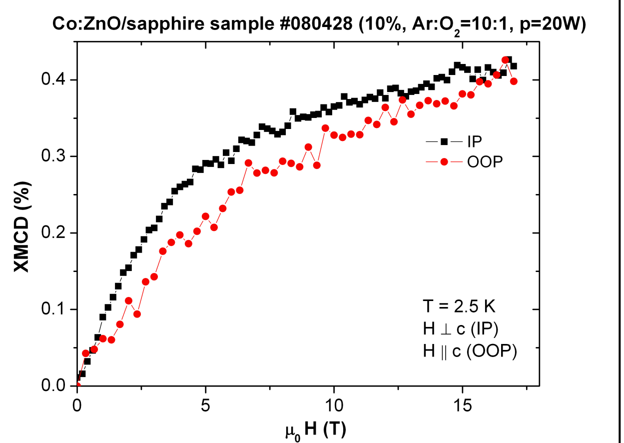

Figure 2: M(H) curves of a PM 10% Co:ZnO film for two different orientations revealing the absence of saturation.

pre-edge feature from -17 T to +17 T (curves were averaged to fit one quadrant). Significantly, the curvature of the M(H) curves is different which is readily explained by the well-known single ion-anisotropy of PM Co^{2+} in ZnO which was not visible in earlier measurements at higher temperatures and lower fields (A. Ney et al. PRB 81 (2010) 054420). However, the M(H) curve at high magnetic fields does not exhibit a characteristic step-like behavior which would be characteristic of a spin-flop transition of AFM Co-O-Co pairs. The signal-to-noise ratio is not sufficient to judge if the kink just below 15 T may represent the indication of such a transition. On the other hand, both M(H) curves do not saturate up to 17 T which is in contrast to the expectations of PM Co^{2+} in ZnO. Since in this sample contains 10% Co, larger Co-O-Co-O… configurations are present as well. The finite slope of the M(H) curve can thus be interpreted as the breaking up of the AFM alignment of these larger configurations which presumably have a reduced effective AFM coupling compared to the Co-O-Co pairs. In any case, the finite slope of the M(H) curve up to 17 T is a direct evidence of AFM interactions in these samples and it cannot be explained by ferromagnetic interactions of pure PM.

This interpretation is corroborated by studying the M(H) curves for 5%, 10% and 15% Co doped ZnO as shown in Figure 3. It can be clearly seen that both the slope at high magnetic fields as well as the curvature at low magnetic fields is significantly different for the three samples. Note that the curves have been normalized to the XMCD signal at 17 T for ease of comparison. Since this series of samples contains isolated Co ions, Co-O-Co pairs and higher configurations in different concentrations, a detailed quantitative analysis may provide information on the magnitude of the AFM coupling of some of the larger Co-O-Co-O… configurations. However, this required the exact knowledge of the Co concentration which is at present only known as a nominal value.

Finally, Figure 4 displays the comparison between the PM 10% Co:ZnO with two other samples. One is a highly resistive N-codoped Co:ZnO films which is PM as measured by SQUID. The reduced carrier concentration due to the N-codoping can be expected to influence the magnetic interactions as predicted by theory. Indeed, the M(H) curve of this sample exhibits an altered slope at high magnetic field which – following the previous discussion – can be interpreted as an altered magnitude of the magnetic interactions for the lager Co-O… configurations. The increase of the slope of the M(H) curve at high magnetic fields is even more pronounced for the SPM Co:ZnO film which is shown in Figure 4 as well. This again indicated a change in the magnetic interactions of the PM fraction of the Co dopant atoms, since this M(H) curve was recorded at the pre-edge feature. For this film, phase separation was proven (HE-2714 and A. Ney et al. NJP 12 (2010) 013020). Therefore the M(H) curve measured as well at the photon energy characteristic for metallic/elemental Co ad the result is in stark contrast. The M(H) curve quickly saturates below 2 T and is field independent from there-on up to 17 T. This clearly reveals the origin of the SPM behavior of this sample to be Co with metallic/elemental character. The corresponding XMCD spectrum of the SPM sample is in agreement with previously measured ones at 6.5 K and 6 T (HE-2714, not shown here).

In summary, despite the absence of a clear evidence of a spin-flop transition in the M(H) curves at high magnetic fields, the findings on a number of samples provide direct evidence of AFM interactions in Co:ZnO.

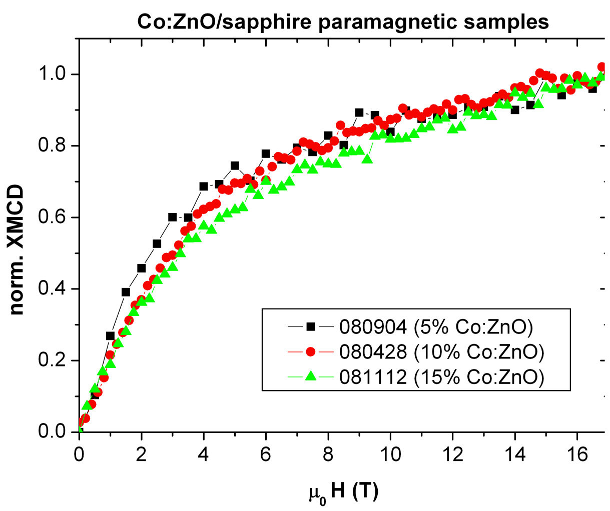

Figure 3: M(H) curves of Co:ZnO films as a function of Co concentration recorded at 2.5 K applying the magnetic field in the film plane ($H \perp c$).

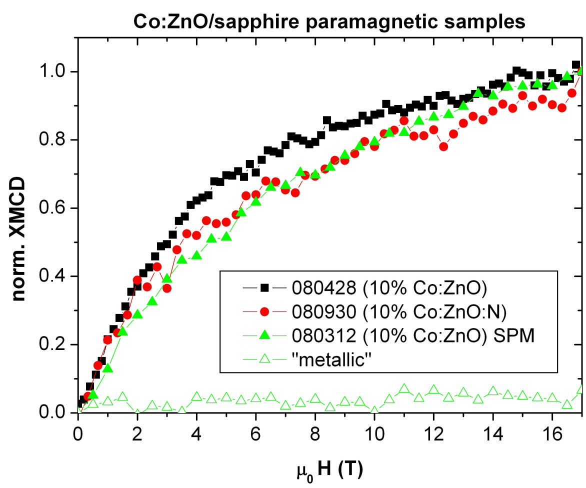

Figure 4: M (H) curves of 10% Co:ZnO films recorded at 2.5 K applying the magnetic field in the film plane for PM Co:ZnO, PM Co:ZnO:N and SPM Co:ZnO. Open triangles show the "metallic" contribution of the SPM sample.