ESRF	**Experiment title:** Magnetic polarization at the Co and Zn sites in ZnO:Co	**Experiment number:** HE-2089
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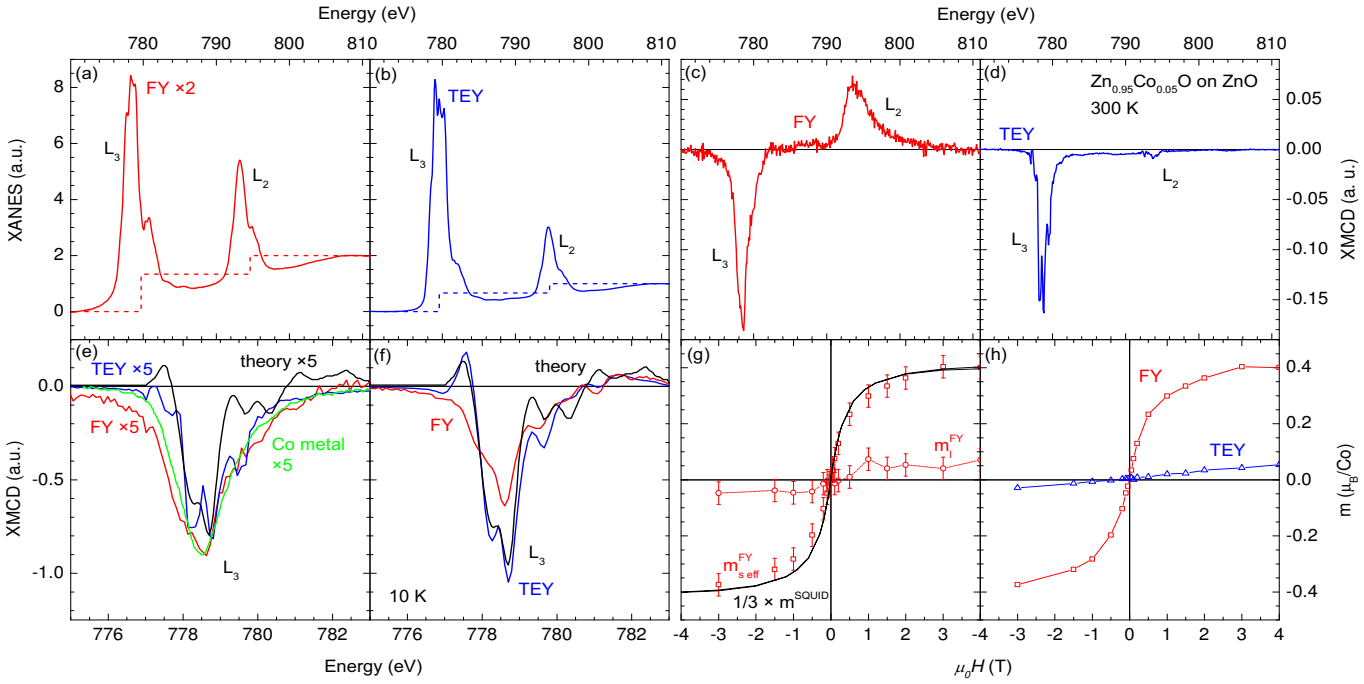
Report:

Diluted magnetic semiconductors are highly notified materials as they combine the versatile electronic properties of semiconductors with ferromagnetic exchange. Due to its Curie temperature T_C above room-temperature [1] cobalt-doped ZnO is particularly interesting for applications. However, the nature of the observed ferromagnetism is still under debate. Especially the occurrence of extrinsic sources such as metallic Co clusters could not yet be excluded. To clarify this issue we have measured x-ray magnetic circular dichroism (XMCD) because it gives information about the microscopic nature of the magnetically active cobalt in our samples.

We have grown (0001) oriented $Zn_{0.95}Co_{0.05}O$ thin films on (0001) ZnO, (0001) Al_2O_3 and (0001) $ScAlMgO_4$ substrates by pulsed laser deposition. The samples were deposited at different temperatures (300, 400, 500, and 600°C) in Ar-atmosphere. X-ray diffractometry showed a very high structural quality of the epitaxial films.

The magnetic properties were measured by SQUID magnetometry and XMCD performed at beamline ID08. We have measured the magnetic moment of the cobalt atoms at the L_2 and L_3 edges in fluorescent yield (FY) and total electron yield (TEY) mode to distinguish between bulk and surface properties. Each measurement consisted of eight consecutive x-ray absorption spectra (XAS) in an energy range from 765 to 815 eV, four of them measured with right (rcp) and four with left circularly polarized (lcp) light. The spectra were normalized to unity with respect to the intensity after the L_2 edge at 810 eV. To compare the results with SQUID $M(H)$ loops, we took the eight spectra at constant fields from 4 to -3 T. In Figs. (a) and (b) XAS scans of a $Zn_{0.95}Co_{0.05}O$ film grown on ZnO at 400°C are shown. The spectra were measured simultaneously in FY (a) and TEY (b) mode at T=300 K and 4 T and

represent averages of the four measurements with lcp and rcp light. Both spectra exhibit a clear multiplet structure at the L_3 edge indicating the presence of Co^{2+} in the samples. In Figs. (c) and (d) the XMCD signals corresponding to the difference of lcp and rcp XAS scans are shown. There is significant difference between FY and TEY mode. While on the L_3 edge of the TEY curve a clear multiplet is visible (d), there is no structure on the FY XMCD signal (c). This multiplet structure on the XMCD signal is the key to understand the microscopic nature of the magnetically active cobalt. Therefore we compare the XMCD signals with a theoretical calculation for tetrahedrally coordinated Co^{2+} in ZnO taken from [2] and a metallic cobalt XMCD spectrum from [3], see Fig. (e). We find that the FY XMCD signal (red) can be well explained with metallic cobalt (green). Comparing it to the theoretical calculation (black) reveals no indication of magnetically coupled Co^{2+}, because the characteristic multiplet structure predicted by theory is not visible. In TEY XMCD (blue) we observed this multiplet structure indicating the presence of Co^{2+} at the surface. In Fig. (f) the same is shown for 10 K. Here the TEY curve nicely follows the theoretical calculation.



By applying the magnetooptical sum rules, the magnetic effective spin ($m_{s,eff}$) and orbital (m_l) moments can be calculated, see Fig. (g), (h). In (g) the SQUID magnetization curve is shown, for comparison. The shape of the magnetization curves obtained by FY and SQUID magnetometry is identical, but the absolute magnetic moments observed by FY XMCD are by a factor of 3 smaller than those determined from SQUID magnetometry. This provides evidence that the whole signal observed by SQUID magnetometry at room temperature originates from metallic cobalt precipitates. The magnetic moments determined from TEY are significantly smaller than in FY (Fig. (h)) and can be well explained with paramagnetic Co^{2+} ions. This result indicates the presence of a magnetically dead surface layer.

[1] K. Nielsen *et al.*, phys. stat. sol. (a), **203**, 3581 (2006).

[2] M. Kobayashi *et al.*, Phys. Rev. B, **72**, 201201(R) (2005).

[3] K. Mamiya *et al.*, Appl. Phys. Lett., **89**, 062506 (2006).