XMCD studies on Co and Li doped ZnO magnetic semiconductors

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Abstract. ZnO doped with a few per cent (<10\%) of magnetic ions such as Co exhibit room temperature (RT) ferromagnetism, transforming it into a very promising candidate for future spin electronic applications. We present x-ray magnetic circular dichroism (XMCD) spectroscopy, which has been used in total electron yield, total fluorescence yield, and reflection mode to investigate the origin of ferromagnetism in such diluted magnetic semiconductor materials in a surface, bulk and interface sensitive way, respectively. We investigated three different types of samples: ZnO doped with 5\% Co, artificially layered films, and layered films with additional co-doping of 10\% Li. These films are prepared by pulsed laser deposition (PLD) and characterized by superconducting quantum interference device (SQUID) magnetometry. Extensive XMCD measurements at the Co L\textsubscript{2,3} and the O K edges, done with a very good signal-to-noise ratio, have revealed only cobalt paramagnetism and non magnetic oxygen signatures at low and high temperatures. We do not see any element specific signature for ferromagnetism at all. By exclusion, our results suggest oxygen vacancies as the intrinsic origin for RT ferromagnetism in doped ZnO.

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1. Introduction

After the theoretical prediction [1] and the first experimental finding of room temperature (RT) ferromagnetism in transition metal (TM) doped ZnO [2], enormous effort has been made to verify the intrinsic presence and the origin of ferromagnetism in such diluted magnetic semiconductors (DMS) [3]. This is based on a very promising combination of material properties, such as semiconducting behavior, transparency and ferromagnetism. Therefore, TM doped ZnO is a very hopeful candidate for future spintronic applications [4, 5]. The recent observation of strong magnetoresistive effects is confirming this perspective [6]–[8]. In terms of DMS some ferromagnetic interaction models [3], such as Zener exchange [1], double exchange [9, 10] and bound polaron model [11]–[13] have been discussed so far. In addition, density functional theory and related supercell calculations have been performed to analyze in detail the magnetic interactions, which find predominating antiferromagnetic (AF) interactions for the undoped ZnO, and small FM interaction if free charge carriers are introduced, for example, by further doping with Al [14]–[16]. This behavior is common, also well known for other types of DMS (for a review see [17]–[19] and references therein). In addition, the presence of oxygen vacancies or TM interstitials has been identified to be important to stabilize and/or destabilize FM in ZnO-based DMS [20]–[22]. However, all these more or less carrier related FM interaction models are based on the assumption that the TM ions are ordered ferromagnetically, and the ordering is mediated via the doping modified ZnO host.

From the experimental point of view, many controversial results have been found so far [3]. One major problem is the variation of the ferromagnetic moment per dopant TM ion. This can vanish without any change in the experimental set-up or even exceed the magnetic moment of the dopant TM ion [3, 23, 24]. The latter point clearly indicates a different source for FM in DMS. On the other hand, FM is present for nearly all TM ions and often quite high for Co doping [25]. These findings clearly question the ferromagnetic role of the TM ion. In fact, TM doping alone does not provide unambiguous FM at all.
As suggested by theory, doping with charge carriers should be able to dramatically influence the FM in DMS, but recent experiments found strong changes of charge carrier densities up to three orders of magnitude with nearly no impact on the FM [26]. In contrast, other non stoichiometric variations have shown strong influence on the ferromagnetism. For example, evaporating and annealing with pure Zn have dramatically enhanced FM and subsequent annealing with oxygen resulted in vanishing FM [27]–[29]. Similar on–off switching behavior has been reported by annealing with hydrogen [30]–[34], which has also been attributed by infra red spectroscopy as a mediator for oxygen vacancies [33, 35, 36]. Likewise, enhancement of FM has also been observed by film preparation under reduced O partial pressure or thermal annealing under vacuum conditions [37, 38]. Zn metal and H treatment and also the vacuum annealing processes enhance the number of O-vacancies and also the RT-FM in such samples, clearly suggesting the importance of O-vacancies to the RT-FM in ZnO [20]. Very strong effort must be made to verify the absence of TM clusters, which have been proposed as another possible extrinsic explanation for the variation of FM properties in such materials [39]. The majority of recent publications have clearly found by a variety of methods, at moderate TM concentrations, that the TM are in fact substituted on the tetragonal Zn sites, and are in a TM$^{2+}$ configuration. This has been shown for example by x-ray absorption spectroscopy (XAS) [21, 32], [40]–[43], x-ray emission spectroscopy (XES) [21], x-ray magnetic circular dichroism (XMCD) [40, 41, 42, 44], x-ray photoelectron spectroscopy (XPS) [45], electron paramagnetic resonance (EPR) [16, 46, 47], extended x-ray absorption fine structure (EXAFS) [48, 49], and Rutherford back-scattering (RBS) [50, 51].

Very striking results have found FM in undoped ZnO [52, 53], and also in ZnO doped with typical non magnetic ions [54] like carbon [55], Sc [56], Cu and Al [56, 57], and implanted Ar [58], also finding a strong dependence of the FM on the number of vacancies. These observations clearly call the role of TM of the TM ions into question.

Since its discovery, XMCD has become a unique and widely used tool to study quantitative and element specific magnetic moments in complex systems [59, 60]. XMCD is the magnetism induced change in the absorption coefficient, which could be used to probe the projected magnetism, for example of the TM ion 3d shell. This magnetism related change in the absorption spectra appears close to an absorption edge, where resonantly excited core electrons probe the unoccupied density of states (DOS). XMCD utilizes circular polarized photons, which probe the magnetism of the unoccupied states. The overall magnetic polarization of the unoccupied states is in one to one correspondence with the magnetic properties of the occupied density of states. Due to the so-called dipole selection rules and the local character of the core electrons, symmetry selective and element specific magnetization projections could be investigated. For example, the $2p \rightarrow 3d$ excitation at the 3d TMs probes the projected magnetism of the d-orbitals, which overlap with the core $2p$ electrons. Due to the fact that the binding energy of the $2p$ electrons is modified for different nuclear charges, the resonant excitation appears at different photon energies. For example, the Fe $2p \rightarrow 3d$ threshold is at 707 eV, while the corresponding Co transition appears at 778 eV (see for example figure 2). These symmetry and site selective changes of the absorption coefficient are proportional to the difference of the projection of the magnetization along the circular polarized photon beam direction. This effect is maximized by switching between parallel and antiparallel aligned sample magnetization with respect to the photon beam, which is the usual measurement mode in XMCD spectroscopy. In addition, XMCD allows the separate and quantitative determination of spin and orbital
projections via sum rules [61]–[63]. In the case of ferromagnetically ordered Co, one would expect a XMCD related asymmetry in the absorption signal in the range of 30–50% [61]. For the non expert reader and further details about XMCD, we would like to refer to some basic publications [64]–[68] and books [69, 70].

In order to identify the FM ion, previous element specific XMCD measurements have been performed at the TM L_{2,3} edges. First XMCD results at the Co L_{2,3} edges have found a mixture of AF like magnetism and a very small ferromagnetic Co magnetization [44]. More detailed XMCD measurements by Gacic et al [40], performed at different temperatures and magnetic fields, have recently found no indication for long range Co magnetic ordering above 5 K, but some indication for weak AF coupling. In addition, no magnetic moment has been found at the Zn ions [40]. These findings have been quantitatively confirmed by detailed high-field and low-temperature vibrating sample magnetometry (VSM) measurements, where the paramagnetic moment is equivalent to the total amount of Co present in the sample. This clearly suggests that Co is only paramagnetic at RT even in the bulk of the doped ZnO sample. Recent XMCD results from Barla et al [41] confirm these findings. Similar small XMCD effects (not quantified) have been found for Mn doped ZnO [42]. It should be mentioned that all these XMCD experiments have been performed in the more surface sensitive (1–5 nm sampling depth) total electron yield (TEY) mode. Therefore, one question arises: is the absence of TM–FM related to a non FM surface layer, while the FM is located below? This question could be answered by bulk sensitive methods, like XMCD in total fluorescence yield (TFY) or reflection (XRMR — x-ray resonant magnetic reflectivity) mode, as will be addressed here.

In order to find the FM element in doped ZnO, Co L_{2,3} and O K edge XMCD experiments have been performed for slightly (5 at. %) Co doped samples. Moreover, two additional sample types have been prepared to enhance FM: one with inner interfaces by sequential deposition, and one with Li co-doping as suggested by Sluiter et al [71]. Sum rules have been applied, to obtain quantitative additional information for orbital and spin magnetic moments [62, 63]. This is now a well-established method for element specific magnetometry [65, 69, 70].

Even by very time consuming ultra low noise surface, bulk, and interface sensitive XMCD measurements, no element selective indication for FM has been found in the investigated samples, for any TM ion or for oxygen. As the possible remaining source for FM, we suggest by exclusion that O-vacancies are most likely to be responsible for RT-FM in ZnO.

2. Experimental

All samples were grown on 5 mm × 5 mm r-plane sapphire (1–102) substrates by pulsed laser deposition (PLD) using a KrF excimer laser with a wavelength of 248 nm. Zn_{0.95}Co_{0.05}O and Zn_{0.85}Co_{0.05}Li_{0.1}O targets were prepared by conventional solid state reaction method. Powders of ZnO, Co_{2}O_{3} and Li_{2}O, respectively were mixed together, subsequently pressed and sintered for 12 h at 1000 °C in air. The films were deposited in vacuum at a pressure of around 10^{-6} mbar and a laser energy density below 2 J cm^{-2}. At a substrate temperature of 600 °C and a deposition rate between 1 and 2 nm min^{-1} we produced films with a thickness of typically 50 nm. In order to avoid external impurities, the sample holder has been covered by a non magnetic molybdenum plate before mounting the substrate. Only non magnetic titanium tweezers have been used during the whole work. Hence, there should be no magnetic impurities on the edges or the bottom of the substrates. Also, no ferromagnetism has been found for control samples.
of undoped ZnO which were deposited under the same conditions. Transmission electron microscopy (TEM) measurements were performed earlier for similar samples and no indication of metallic Co clusters was found [40].

Trying to adjust the deposition parameters in order to maximize the ferromagnetism of our samples we found that there is a narrow laser energy and temperature range where most of the deposited samples showed ferromagnetic behavior. Small changes of the energy density or the temperature led to a strongly decreasing or vanishing magnetization. Another way found to increase and stabilize ferromagnetism is to deposit several layers of the same compound at different temperatures. It is assumed that some kind of inner interfaces or regions with a high defect density are generated this way. These, in the following referred to as ‘triple layered’ samples, were deposited at layer-temperatures of 600 °C/500 °C/400 °C in this order from bottom to top. Other conditions were kept the same. X-ray diffraction measurements have clearly shown an increase of disorder and a reduced epitaxy for the triple layered as well as for the Li co-doped samples. We will show results on three different samples. A single layer just doped with 5% Co, a triple layer 5% Co doped sample referred to as ‘triple layered’, and a triple layered 5% Co doped sample co-doped with 10% Li referred to as ‘Li co-doped’ or ‘Li doped’.

The XMCD and XAS measurements were performed at the bending magnet beamline PM III at BESSY II in Berlin. The energy resolution of the beamline was set to about $E / \Delta E = 5000$. All results have been corrected for the degree of circular polarization, which was $92 \pm 4\%$. Field-dependent XAS and XMCD spectra were taken in the TEY-mode. Additionally, in order to probe bulk like properties, we performed nonmagnetic and magnetic TFY measurements in remanence and field-dependent resonant reflectivity measurements (performed at BESSY UE56-2 undulator beam line of the Max-Planck-Society). For the XMCD measurements (TEY and TFY) we used a fast switching superconducting magnet system which is able to flip the sign of the magnetic field from $-2 \, \text{T}$ to $+2 \, \text{T}$ in less than 6 s. To minimize electronic- and synchrotron-based drift phenomena, we have obtained maximum sensitivity by flipping the external magnetic field at each energy data point. For the RT measurements a sensitivity of the XMCD signal up to $10^{-5}$ with respect to the full absorption signal could be achieved. At low temperatures the signal-to-noise ratio is reduced by about one order of magnitude due to small thermal fluctuations of the L–He cryostat. This high sensitivity allows us to determine very small element specific magnetic projected spin and orbital moments even for the diluted TM ion down to approximately $10^{-4} \mu_B$ ($10^{-5} \mu_B$ for pure TM). The energy of the spectra has been calibrated to the Co L$_{2,3}$ edge results previously published in [40]. The absorption measurements have been performed in normal incidence geometry, to minimize non XMCD related differences (offsets) in the XMCD spectra [72, 73]. These offsets were smaller than 0.1% with respect to the total absorption signal and have canceled each other nearly perfectly by averaging the experimental data for both light helicities. Further experimental data treatment has been discussed and shown elsewhere [73]. We have also performed angular-dependent TEY measurements (not shown) to check for anisotropic magnetic absorption properties, which have not been observed. Therefore, we will neglect in the following magnetic dipole term contributions $T_z$, which are also present in the effective XMCD spin, if the local symmetry is less than cubic [62, 74].

The soft x-ray reflection mode measurements have been performed with our new soft x-ray diffractometer, which will be described in detail elsewhere.
3. Results

3.1. SQUID

SQUID measurements at RT and at low temperatures showed clear ferromagnetic behavior (figure 1). As mentioned before, the magnetic properties are extremely sensitive to the preparation conditions, which is the main reason for the bad reproducibility that is often reported. The magnetization of our samples varied between 0.1 and 2 $\mu_B$/Co. Usually the remanence is about 10% of the saturation magnetization and the coercive field is below 10 mT at 300 K, but a few samples, especially the triple layered and Li co-doped, exhibit a much stronger remanence and coercivity. While the triple layered samples also showed improved reproducibility, the reproducibility of the Li co-doped samples is worse, but the magnetization, remanence and coercivity of a few samples are extraordinarily high. The best samples (Li co-doped) show a saturation magnetization of 2.05 (1.81) $\mu_B$/Co, a remanence of 1.38 (1.24) $\mu_B$/Co and a coercivity of almost 200 (100) mT at 2 K (300 K). The remnant magnetization of these samples is well suited for our remnant TFY measurement, which will be shown and discussed later on.

3.2. Co $L_{2,3}$ edge absorption spectra

3.2.1. TEY. Figure 2 shows the XAS (RT) and XMCD spectra (RT and 15 K) at the Co $L_{2,3}$ edges for the single layered Co doped, the triple layered Co doped and the Li co-doped samples. These absorption edges are due to a Co 2p $\rightarrow$ 3d transition, which provides information on the unoccupied density of the Co 3d states, probing the projected 3d magnetism of Co. The shape of the XAS and XMCD spectra is not affected by the Li doping and/or the layering significantly. Nevertheless, Li doping provides a tiny shoulder at the low energy site of the Co $L_3$ edge at about 778 eV, indicating the doping related depopulation of states close to the Fermi level. In addition, a theoretical XAS multiplet spectrum of Co in tetrahedral coordination (Co 3d$^7$ in $T_d$...
symmetry) is reproduced for XAS and XMCD from [41] in figure 2. The shape of the shown Co L$_{2,3}$ spectra is nearly identical to the tetrahedral multiplet spectra, providing a consistent description of Co ions located at the Zn site in tetrahedral coordination (see the introduction) [16, 21], [45]–[51]. This is the expected site symmetry and valence for Co ions located at the Zn site and also consistent with other recently published XMCD results on single layered Co doped ZnO [40, 41]. Our results show that Li doping and inner interfaces do not change the electronic configuration and the local symmetry of Co significantly.

In addition, the RT XMCD 2 T spectra for the undoped (reproduced from [40]), the triple layered, and Li co-doped samples are shown in figure 2(b). The shape and the amplitudes are nearly the same, directly suggesting similar magnetic moments and temperature dependences. We have performed the same sum rule analysis as in [40] (assuming a Co$^{2+}$ 3d$^7$ configuration $\rightarrow n_h = 3$) for the triple layered and Li co-doped samples. The magnetic moments and spin/orbit ratios are equal. All samples provide a non vanishing orbital moment of about 25%, respective to the spin moment. This observation combined with the clear multiplet-like shape of the XAS and XMCD spectra proves the absence of metallic Co in the surface near region (TEY). Metallic Co clusters would exhibit strongly different spectral shapes and nearly quenched orbital moments.

To obtain the element specific Co magnetization behavior, the L$_3$ edge region of the Li doped sample has been measured in TEY mode at 15 K as a function of the external magnetic field (similar to the single layered Co doped sample). To extract the field-dependent magnetization values, shown in figure 3, the integral value of the L$_3$ edge region has been scaled to the sum rule values obtained from the full spectrum shown in figure 2 [40]. To enhance the visibility positive values are multiplied by $-1$ and extended to the negative region. No sign of ferromagnetism could be observed even at low temperatures.
Figure 3. Co L₃ edge XMCD related magnetic spin moment for the Li co-doped sample as a function of the external field. For better visibility the data have been extended to the negative region. The inset shows the 2T temperature dependence for the 5% doped sample (hollow squares), extracted from [40] combined with the corresponding Li co-doped XMCD results (blue triangles).

The absolute Co moments, as shown by blue triangles in the inset of figure 3, are quite the same as observed for the single layered sample temperature dependence from [40] (pure Curie–Weiss behavior with no ferromagnetic component). The triple layered sample provides the same values (for better visibility not shown).

As a conclusion, also for the triple layered and the Li co-doped samples only paramagnetic behavior of the Co sublattice magnetization has been found in TEY–XMCD measurements.

3.2.2. TFY. Due to the fact that TEY spectra are rather surface sensitive with an effective sampling depth of 1–5 nm, only near surface regions have been investigated by the measurements presented so far. To exclude that the paramagnetic behavior is just a surface effect, for example due to oxidized metallic Co clusters, we have performed TFY spectra.

Figure 4(a) shows TFY XAS spectra for the Li co-doped (300 K) and the triple layered sample (for both magnetization directions at 15 K). Despite the higher noise level in TFY mode, it is clearly visible that for all samples the shape of the TFY yield spectra is in nearly perfect agreement with the multiplet-like TEY spectra shown above in figure 2. It is evident that no Co-metal-like clusters are hidden below the surface.

Figure 4(b) shows the TFY 15 K XMCD data of the triple layered sample. For this measurement the magnetization has been flipped by an external field of 2 T at each data point, similar to the TEY measurements, but immediately tuned to zero before the fluorescence measurement. This procedure has been chosen for two reasons. The first reason is related to our experimental setup, because the FY detector provides higher noise levels in applied magnetic fields, and the second reason is to clearly identify just the ferromagnetism, which should provide reasonable magnetic moments at low temperatures (≈ 0.5 µ_B/Co, see SQUID data above). If FM is really related to Co magnetic moments one should see a sizable magnetic XMCD effect. Nevertheless, no magnetic TFY signature could be seen above the noise floor. By comparing
the noise floor with the white line intensity and the TEY XAS–XMCD results, we provide an upper estimate for the maximum FM-remanent-magnetic-moment per Co ion of less than 0.015 $\mu_B$/Co. This value is about two orders of magnitude smaller than the SQUID related magnetic moment per Co, but consistent with the above discussed TEY XMCD magnetization measurements, where no remanent XMCD effect would be expected.

Therefore, we can conclude with no doubt the clear absence of FM–Co in our samples. In addition, also the TFY spectra do not provide any indication for a remanent magnetization of Co below the surface and/or Co metal like clusters.

3.3. O K edge absorption spectra

3.3.1. TEY. Figure 5(a) shows the oxygen K edge TEY–XAS spectra of the above discussed three different samples. The spectra for the Co doped triple layered and single layered samples are quite close to each other and in very good agreement with other doped ZnO O K edge XAS results published so far (Co: [21, 43]; Mn: [42]). The main O K edge region from 533–538 eV has been identified as O 2p states hybridized with Zn 4s states, while the maximum at about 537 eV is related to more localized O 2p$_z$ and 2p$_{x+y}$ states [21, 43]. The high energy region up to 550 eV is dominated by O 2p–Zn 4s hybrid states. TM doping gives a low energy double feature shoulder close to the transition threshold reflecting the doping induced reduction of the band gap. This low energy structure is originated by a shift in the 1s–2p onset energy and identified as induced by oxygen vacancies [43]. From figure 5(a) the Li co-doped spectra show strongly enhanced double structured features compared to the just TM doped samples, which are now clearly visible as double peaks. In addition, the localized structure at 537 eV is smeared out and shifted to higher energies, indicating an increased dispersive character.

Figure 5(b) shows the strongly magnified corresponding O K edge XMCD spectra. These spectra do not provide any significant structure above the noise floor. We have performed a very
large number of XMCD spectra at the O K edge at both temperatures (RT and low temperature). For all measurements no significant and reproducible structure has been observed, even for the Li co-doped samples. The shown RT results provide our optimal signal-to-noise ratio of less than 0.05% compared to the O K edge jump, which is less than $1 \times 10^{-5}$ with respect to the total XAS signal.

3.3.2. TFY. Comparable to the above described TFY Co L$_{2,3}$ spectra, we have performed O K edge measurements to gain bulk sensitive information.

Figure 6(a) shows TFY XAS spectra (for both magnetization directions of the triple layered sample) measured at a temperature of 15 K. Similar to the above shown comparison of the Co L$_{2,3}$ TFY and TEY spectra, the shape does not change dramatically. Only the double peak like structure of the Li co-doped sample is modified in the TFY signal. However, some spectral contribution is related to the oxygen from the substrate. Therefore, we will not discuss spectral shape differences of the O K edge TFY in detail. This is also not as important here, because we focus on the O 2p magnetic polarization.

Figure 6(b) shows the 15 K XMCD O K edge data of the triple layered sample, performed in remanence as explained above for the Co L$_{2,3}$ TFY spectra, but with a better signal to noise level and experimental statistics compared to the Co L$_{2,3}$ TFY spectra shown above. If the FM is really related to oxygen magnetic moments one would expect a sizable magnetic XMCD effect (see discussion below). Nevertheless, no magnetic TFY signature can be found above the noise floor. Similar to Co we do not see any element-specific FM in the O K TFY XMCD spectra.

3.4. Co L$_{2,3}$ and O K edge magnetization in reflection mode

In the past, the influence of the interface at the substrate and the ZnO film on the FM has been discussed in terms of induced structural disorder, lattice mismatch and stress (see [3, 23] and references therein). In order to find any element specific signature of interfacial FM,
we have performed XMCD measurements in reflection for the single layered Co doped sample. This method provides bulk information and is even more sensitive for interface related magnetism [75]–[79]. Field-dependent reflectivity curves at fixed angle of incidence have been performed at the energy of the Co L_{3} edge XMCD maximum and at the first O K edge peak. This technique is also known as soft x-ray Kerr magnetometry [80].

The reflection measurements have been performed at RT. The Co L_{3} reflection mode XMCD (i.e. XRMK) magnetization curve is shown in figure 7(b). No FM signature could be found. A small finite slope could be vaguely identified, corresponding to the Co paramagnetic moment, which is about 0.003 \( \mu_B \) at the applied field of 150 mT (estimated from the paramagnetic results shown above).
A similar O K edge experiment with improved statistics is shown in figure 7(a). This measurement has been performed with a high integration time and increased intensity to obtain a one order better signal-to-noise ratio as compared to the Co measurements shown in figure 7(b). Again, no signature for FM has been found. We also have performed magnetic energy-dependent reflection measurements with fixed momentum transfer and magnetic reflectivity measurements, both at the Co L3 XMCD maximum and the O K edge onset region (not shown). In these cases the magnetic field has been flipped at each data point between ±150 mT to obtain maximum sensitivity and saturation. Again, no magnetic asymmetry has been found in the noise level of less than $10^{-3}$, for Co and O.

4. Discussion

Due to the fully unexpected absence of ferromagnetic element specific signatures, we now briefly recapitulate the results. This absence will be discussed in more detail for each element separately, in order to find a possible explanation.

Single layered Co doped and Li co-doped ZnO thin films have shown well-defined FM behavior in SQUID magnetization loops. The FM moment was in a range up to $2 \mu_B$/Co ion. This absolute value of the ferromagnetic moment is quite good, compared to the many other results published so far. Nevertheless, by the use of element specific XMCD magnetometry, no sign of FM has been found at the Co L2,3 and the O K edges of single layered Co doped, artificially triple layered and also additionally Li co-doped ZnO. Li and layering have been used to successfully increase the FM behavior (SQUID), especially the remanence and the coercive fields. Nevertheless, all shown experiments, surface, bulk and interface sensitive, have only found very small XMCD effects at the Co L2,3 edges, which are in perfect agreement with paramagnetic Co moments with no indication of FM or remanent magnetization. In addition, very sensitive, careful and time consuming measurements have been performed at the O K edge, with no sign of magnetism at all. Unfortunately, Li has no absorption edge suitable for XMCD, which has not been investigated here. In addition, also Zn L2,3 XMCD spectra have not shown any signature for FM at all [40].

This results in a very puzzling situation that FM has been found by magnetometry, which could not be related to any element present in the sample. In the following we extend the discussion separately for each element.

4.1. Cobalt

Co could be clearly excluded as an origin for FM in such systems. If the magnetization observed in the SQUID measurements of up to $2 \mu_B$/Co is in fact originated by Co, XMCD asymmetries in the order of 10–50% should be observed at the Co L3 edge, even at RT. The observed asymmetry was orders of magnitude smaller in any measurement mode (TEY, TFY and reflection). The spectral shape (TEY surface and TFY bulk sensitive) was perfectly reproduced by theoretical spectra of Co$^{2+}$ incorporated at the tetrahedral Zn site and also consistent with previous XAS (XMCD) results, with no indication of metallic-like Co clusters. This shows that the samples are homogeneous, with no extrinsic Co cluster like magnetization located below the surface and/or the interface.
4.2. Oxygen

The O K edge measurements do not show any indication for oxygen magnetization at all. It should be mentioned that a large number of O K edge XMCD spectra have to be measured, each under optimal conditions with increased integration time, to achieve such a high sensitivity and signal-to-noise ratio. It is also necessary to measure pairs of XMCD spectra with opposite helicity, during the same injection run at the synchrotron, under exactly the same conditions of energy step size, delay times, etc, to perfectly remove residual small side effects.

Now we compare the O K edge results to other known FM oxide systems. One of the most prominent FM oxides is CrO$_2$. For CrO$_2$ a relatively large XMCD effect at the O K edge of about 4% with respect to the corresponding O K edge XAS signal has been found. The related O 2p magnetic moment has been recently calculated to be about $-0.16 \mu_B$ [81] and $-0.145 \mu_B$ [82]. Therefore, the XMCD asymmetry (XMCD/XAS) per magnetic moment at the CrO$_2$ O K edge could be determined to be about $0.27/\mu_B$.

If we now attribute the FM magnetization in Co doped ZnO of about 1.4$\mu_B$/Co to oxygen by recalculating the total magnetization, we obtain an oxygen magnetization of $1.4\mu_B$/Co $\times$ 0.05 Co/1.00 oxygen = 0.07$\mu_B$ per O ion. This is comparable to the magnetic moment of O in CrO$_2$ suggesting roughly the same order of magnitude of the XMCD effect at the ZnO O K edge. The emerging question is: why do we not see any O K edge XMCD in our doped ZnO samples, if the magnetization per oxygen ion is comparable to CrO$_2$?

Two explanations could be given. The first and of cause trivial answer is, there is no magnetic moment at oxygen. If not, where does the FM behavior of the sample come from? The second answer is more complicated. It is well known that O K edge XMCD is only sensitive to the O 2p magnetic orbital polarization of the unoccupied 2p DOS [67]. But the magnetic orbital polarization, i.e. the angular moment related contribution of the magnetic moment, of oxygen is a complex property. It is related to the degree of orbital momentum quenching present in cubic symmetry, which is, for example, not perfect, if the local symmetry is less than cubic [83, 84]. This symmetry breaking occurs for two possible reasons, the O spin moment related 2p shell spin–orbit interaction and/or the reduced crystal symmetry. In the case of CrO$_2$ the cubic crystal symmetry is broken and the O 2p shell is strongly hybridized with the Cr 3d orbitals. This results in an orbital polarized band structure, where the complex orbital polarization (two opposite signs) is consistently visible in the Cr L$_{2,3}$ [85] and the O K edge XMCD spectra [86]. The Cr 3d magnetic orbital polarization in CrO$_2$ and the magnetocrystalline anisotropy are then given by the ratio between the spin–orbit interaction and the crystal field (bandwidth) [87]. This situation is completely different in the case of Co doped ZnO. As we have shown above, the Co XAS and XMCD spectra clearly exhibit multiplet-like features. The Co orbital moment is not quenched at all and the magnetic Co 3d electrons behave as well-localized non interacting magnetic moments. Due to the fact that no FM has been found at the Co site no FM orbital polarization could be induced in the neighboring oxygen ions, by randomly oriented nonmagnetic Co. Compared to 3d TM ions like Cr the 2p spin–orbit interaction is reduced. Nevertheless, from the observed noise level, we can clearly estimate any possible oxygen K edge XCMD signal to be smaller than 1/3000 with respect to the low energy (pre edge) structure. This provides a maximum estimate of O K edge asymmetry per O 2p spin moment of about 0.003/$\mu_B$, which is at least 100 times smaller compared to the CrO$_2$ asymmetry per O 2p spin moment (see above). It seems to be very unlikely that the magnetization at the oxygen in CrO$_2$ and ZnO has about the same value but the XMCD effect is two orders of magnitude smaller in
ZnO compared to CrO$_2$. Nevertheless, it is in principle possible to have a local spin polarization with nearly no orbital polarization and related absence of an O K edge signal [88].

Nefedov et al [89] have published recently O K edge asymmetries for TiO$_2$ with implanted Co. These authors found corresponding FM element specific Co and O hysteresis loops by field-dependent XRMR, where the Co asymmetry was about 22% and the O K edge asymmetry was smaller by a factor of 100. Without discussing the presence (in this reference) of Co clusters and related induced FM oxygen in the vicinity of Co clusters, this result clearly shows the sensitivity of XRMR for similar materials and presence of oxygen magnetism. Just by comparison, if FM Co clusters and/or O were present in our samples, we should have seen FM hysteresis behavior in our XRMR experiments, which have at least the same signal-to-noise ratio as demonstrated for the doped TiO$_2$ system [89].

4.3. Zinc

As shown in an earlier paper, no Zn L$_{2,3}$ XMCD has been observed [40, 41]. This was the most promising absorption edge for measuring a possible Zn magnetic polarization. Although, the supposed 3d$^{10}$ configuration of Zn is of course non magnetic. The idea behind this is that a hybridization of the Zn 3d–3p states leads to a small depopulation of the 3d$^{10}$ configuration, which is also magnetized if Zn is magnetic [40, 41]. If ever Zn is FM and we assume in a Gedanken experiment again that the observed FM moment is just provided by the Zn, we would have $1.4\mu_B$/Co $\times$ 0.05 Co/0.95Zn $\approx$ 0.08$\mu_B$/Zn ion. This is again a sizable magnetic moment, which should be visible at the L$_{2,3}$ Zn edge XMCD, because the experiment was performed with such a high signal-to-noise ratio. Nevertheless, no XMCD signal at the Zn L$_{2,3}$ edges has been observed so far, clearly suggesting the absence of Zn magnetization [40, 41].

For doped ZnO no element could be identified in terms of FM. If we now believe that this is in fact true, we just can propose two different explanations, both very unlikely. The first explanation is that all FM measurements performed on TM cluster free samples are based on an unknown extra FM component, for example scratches of iron pincers, diffusion of FM ions into the bottom of the substrate etc. This is of course very unlikely, because all groups working in this field are aware of this problem and much effort has been done to prevent such extra FM contributions. The second explanation is based on oxygen vacancies. These defects can occur with a very high density in ZnO. Lany and Zunger [90] calculated a high density of O vacancies leading to a nonstoichiometry up to 1% for ZnO crystals grown at high temperatures. As PLD grown films represent a growth mode far from thermodynamic equilibrium, an even higher defect density in the films can be expected. Also in ion beam sputtered ZnO films the presence of a very high density of O vacancies up to $10^{21}$ cm$^{-3}$ was concluded using experimental and simulated x-ray absorption near edge spectroscopy (XAS) spectra [31]. The oxygen vacancies do not act as shallow donors but as traps for electrons [90].

As mentioned in the introduction and shown recently, the absence or reduction of O vacancies gives a reduction in the FM moment of doped ZnO samples, clearly demonstrating the importance of such vacancies in terms of FM [52]–[58]. One could speculate that these vacancies themselves are partially occupied by magnetic electrons, which are also FM coupled to each other as proposed by Coey et al [24] for doped ZnO and by Hong et al [91] for doped HfO$_2$. If this is in fact true, the XMCD spectroscopy cannot be used as a probe for such vacancy related magnetism. The reason is that without the presence of a positively charged nucleus no element specific resonant soft or hard x-ray excitation could be performed.

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We would like to mention that the overall reproducibility of the FM observed in doped ZnO was in the range of 10–50%, strongly depending on the preparation conditions. Especially the laser pulse energy is in a very narrow range, to get FM samples. We also tried undoped ZnO films, and carbon doped films, which have not shown FM so far. Both observations will be discussed in more detail elsewhere. From this study one can conclude that FM is preferred for TM doped samples, even without a FM moment at the TM site, suggesting that the possible oxygen vacancy related FM is supported by the TM ion itself.

Unfortunately, theoretical papers on the FM of doped ZnO are focused on the FM interaction of the magnetic TM dopant ions, which are clearly not FM in the samples investigated here. Based on our findings we clearly suggest spin polarized theoretical calculations of undoped ZnO, with the presence of oxygen vacancies to provide possible explanations for the FM in ZnO.

5. Summary

We have performed detailed XMCD measurements on the Co L$_{2,3}$ and the O K edges in order to find the origin of the FM in diluted magnetic semiconductor ZnO samples. Three different types of PLD prepared samples were subject to this investigation: single layered, triple layered and Li co-doped ZnO samples all doped with 5% Co. These experiments have been performed with enhanced surface (TEY), bulk (TFY) and interface (reflection) sensitivity. Only paramagnetic Co has been found, with no sign of FM at all. In all cases and for all types of samples investigated, only spectra have been observed which are consistent with a multiplet description of a Co 3d$^7$ configuration in tetrahedral coordination. This is expected for the substitution of the Zn ions by Co. No indication in TEY and TFY of the presence of Co metal-like clusters has been found. Oxygen FM has been excluded down to extremely small values. We can definitely and without any doubt exclude Co as a possible origin of FM in such systems. Without finding any element-specific signature of FM, we suggest oxygen vacancies as a possible carrier for FM in doped ZnO.

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