Magnetic properties of sol-gel-derived doped ZnO as a potential ferromagnetic semiconductor: a synchrotron-based study

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Abstract. A variety of x-ray techniques is employed to investigate sol-gel-synthesized Co- and Mn-doped ZnO films. X-ray diffraction (XRD) shows that the dominant structure is the $c$-axis orientated wurtzite ZnO. Dopant K-edge extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) indicate that the Co and Mn ions are fourfold co-ordinated with valency $2^+$/3+ and $3^+$/4+, respectively. Surface-sensitive dopant L-edge XANES and x-ray magnetic circular dichroism (XMCD) for the Co dopant are well described by atomic multiplet calculations for tetrahedral Co$^{2+}$, while for Mn the data indicate that the symmetry is lowered due to Jahn–Teller distortion. The XMCD show conclusively that both Co- and Mn-doped ZnO films are purely paramagnetic.

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1. Introduction

Ferromagnetic (FM) dilute magnetic semiconductors (DMS) possess the potential to have a major impact on microelectronics. Consequently, there is a worldwide effort to discover and develop FM DMS that operate at room temperature. At present, the best understood FM DMS are based on Mn-doped III–V semiconductors, including (Ga,Mn)As, (In,Mn)As, (Ga,Mn)Sb and (Ga,Mn)P. These materials show a clear correlation between magnetic and electrical properties and a dependence of the Curie temperature ($T_c$) on dopant concentration that can be understood with existing theories [1]. All of them are ferromagnetic only below room temperature, with the highest reported $T_c$ of 173 K obtained for (Ga,Mn)As [2].

In addition to the confirmed FM DMS, there are many controversial materials, particularly oxides, of which transition metal (TM)-doped ZnO is a typical example and the focus of this paper. A great deal of interest in these materials arose from the prediction of ferromagnetism above room temperature in highly ($p$-type) Mn-doped wurtzite ZnO and GaN [1]. Since then, there have been numerous reports of room temperature ferromagnetism in ZnO:TM, with a great diversity of preparation methods and physical properties [3]. Conversely, many authors do not observe ferromagnetism in this system, or ascribe the ferromagnetism to contaminant phases ([4] and references therein). It is therefore still questionable whether ZnO:TM is a true FM DMS at any temperature.

The ambiguity largely arises from the difficulty in conclusively ascribing the typically small magnetic signal to the TM dopants. For instance, many studies of ZnO:TM rely on bulk magnetometry as principal evidence for ferromagnetism. However, magnetometry involves highly sensitive measurements, which inevitably include the signals from contaminants and dopant-related secondary phases, any of which could be ferromagnetic. Further evidence that the magnetic dopants are actually participating in the ferromagnetism is required, such as: (i) high saturation magnetization close to the expected spin moment, combined with detailed structural characterization confirming that the dopants are uniformly incorporated; (ii) clear demonstration of a relationship between the dopant concentration and $T_c$; (iii) use of an element-specific magnetometry technique to probe specifically the magnetic polarization of the dopant atoms.

X-ray magnetic circular dichroism (XMCD), obtained as the difference between x-ray absorption spectra for opposite magnetization directions with respect to the light helicity vector, is an ideal technique for simultaneously probing chemical and magnetic properties [5]. Since the x-ray absorption spectral lineshape indicates the bonding environment of the dopants [6, 7], the magnetic behaviour can be ascribed unequivocally to incorporated dopants or...
secondary phases, thereby providing direct and conclusive proof of whether a material is an FM DMS.

This paper describes the results of our investigation into sol-gel-prepared TM-doped ZnO as a potential FM DMS.

2. Experimental

The TM-doped ZnO films were fabricated using the sol-gel method. This method was chosen because it is extremely cost-effective for producing the diverse range of structurally ordered samples necessary for an exploratory study. Although a diversity of dopants (and other preparation methods) were eventually employed to study this system, here we focus on Mn- and Co-doped ZnO sol-gel thin films, doped 6 and 3 at.%, respectively, with respect to Zn, the properties of which typify our studies of this system.

The sols consisted of high purity hydrated zinc (II) acetate with hydrated cobalt (II) chloride or manganese (II) acetate dopant sources in appropriate molar proportions, dissolved in dimethyl formamide. Highly c-axis orientated, 50 nm thick nanostructured films were deposited by spin-coating each sol onto hydrophilically terminated sapphire (0001) substrates, as described in a previous publication [8]. A multi-stage annealing regime up to 850 °C was employed to achieve grain growth influenced by the substrate, resulting in the heteroepitaxial relationship {0001} ZnO || {0001} Al₂O₃ and extensive in-plane structural ordering [8].

X-ray diffraction (XRD) measurements were conducted using a Philips PANalytical materials research laboratory x-ray diffractometer with a Cu anode and a β-filtering parafocusing mirror, generating Kα radiation at 1.542 Å. The source was operated at 45 kV and 40 mA, and a parallel plate detector was used. The beam size was 20 mm².

K-edge extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) were undertaken at beamlines 7.1 and 9.3 at the SRS, Daresbury Laboratory, UK, and beamline ID26 at the ESRF in Grenoble. The films were measured at the dopant K-edges in fluorescence mode. High purity powdered reference materials were mixed with about one-third boron nitride powder (by volume), then uniformly spread and enclosed in clear adhesive tape. TM Co and Mn K-edge spectra of the powders were measured in the transmission geometry. At the SRS, this included an in-line absorber metal foil and a third ion chamber to simultaneously monitor the energy scale. The energy scales of spectra measured on different occasions were aligned using these metal foil reference spectra. Zn K-edge data were obtained from the Farrel Lytle database [9]. SRS K-edge data were processed using the Daresbury programs EXCALIB and EXBACK. Analogous ESRF data were processed using EXODUS and WinXAS. All EXAFS data were fitted using the Daresbury program EXCURV98 employing the rapid curved wave scattering theory [10].

Dopant L-edge XANES and XMCD data were measured at 6 K on beamline ID08 at the ESRF using 99 ± 1% circularly polarized light. All the spectra were measured in total electron yield (TEY) mode. A field of up to ±5 T was applied parallel to the photon helicity and perpendicular to the sample plane using a liquid helium-cooled superconducting magnet. Theoretical L-edge XANES and XMCD were calculated following the method described in [7]. The theoretical L₂,₃ absorption spectra were obtained from the electric-dipole allowed transitions between the ground state 3dₙ (Co d₆ and d⁷ and Mn d₃, d⁴ and d⁵) and the corresponding final state 2p⁵3dₙ₊₁ configurations. The wave functions of ground and final states were calculated in intermediate coupling using Cowan’s Hartree–Fock code.
Figure 1. (A) XRD pattern of ZnO powder [11] and sol-gel films: (B) undoped; (C) Co-doped; (D) Mn-doped. Reflections are labelled: 1 = ZnO(0002); 2 = ZnO (1011); 3 = ZnO (1010); 4 = ZnAl$_2$O$_4$ (333); sub. = sapphire {000L}. The spectra are offset for clarity.

with relativistic correction. The Slater parameters, tabulated in [6], were reduced to 80% to account for interatomic screening and mixing. The octahedral crystal field was 10 $D_q = 1$ eV; the tetrahedral crystal fields were $-0.5$ and $-0.6$ eV for Mn and Co, respectively. The exchange field $g\mu_B H$ was 1 meV. The calculated results were broadened by a Lorentzian of $\Gamma = 0.1 (0.3)$ eV for the L$_3$ (L$_2$) edges to account for intrinsic linewidth broadening, and a Gaussian of $\sigma = 0.2$ eV for the instrumental broadening.

3. Results and discussion

XRD patterns of the undoped, 6% Mn and 3% Co-doped films are shown in figure 1 and demonstrate the preferentially orientated wurtzite ZnO structure of the films. The c-axes of both the undoped and Co-doped films are aligned with their substrates since sapphire {0001} and ZnO 0002 reflections (marked ‘sub.’ and peak 1, respectively) dominate the spectra. This alignment is not pronounced for the Mn-doped film, which may be due to the higher doping level for this sample. The ZnO (1011) reflection is also present in all of the films (peak 2); this is usually the most prominent peak in ZnO powder [11]. The ZnO (1010) reflection can also be seen (peak 3); this is the second most prominent peak in ZnO powder. Additionally, a preferentially [333]-orientated ZnAl$_2$O$_4$ phase is barely evident in the undoped and Mn-doped films (peak 4). This phase arises from a solid-state reaction between film and substrate as a consequence of the high annealing temperature necessary to achieve long-range structural ordering [8, 12].

The short-range structural information provided by EXAFS offers an element-specific insight which is complementary to XRD, giving information about the number, position and identity of atoms surrounding the absorbing element, and structural disorder within the coordination spheres [13]. In order to determine the characteristics of these neighbouring atoms, a range of models was systematically applied during fitting. These models included O, Zn, Al, dopant and mixed (Zn, Al, dopant) sites and antisites in all feasible permutations for single and
Table 1. Results of fits to the EXAFS spectra of films shown in figure 2. Reference data [11] are listed for comparison.

| Sample              | Shell    | Radial distance (Å) | Coordination number | Mean squared disorder ($\times 10^{-4}$Å$^2$) |
|---------------------|----------|---------------------|---------------------|-----------------------------------------------|
| ZnO [11]            | Zn–O     | 1.98                | 4                   |                                               |
|                     | Zn–Zn    | 3.21                | 6                   |                                               |
|                     | Zn–Zn    | 3.25                | 6                   |                                               |
|                     | Zn–O     | 3.81                | 9                   |                                               |
|                     | Zn–O, Zn–Zn | 4.57            | 6, 6                |                                               |
| ZnO powder          | Zn–O     | 2.02 ± 0.02         | 3.5 ± 1.4           | 50 ± 50                                       |
|                     | Zn–Zn    | 3.33 ± 0.01         | 21 ± 7              | 180 ± 40                                      |
|                     | Zn–(Zn$_{0.5}$O$_{0.5}$) | 4.69 ± 0.03    | 34 ± 33             | 220 ± 130                                     |
| Co-doped film       | Co–O     | 1.94 ± 0.01         | 4.1 ± 0.3           | 260 ± 20                                      |
|                     | Co–Zn    | 2.57 ± 0.01         | 8.8 ± 2.8           | 690 ± 90                                      |
|                     | Co–Zn    | 3.24 ± 0.01         | 0.7 ± 0.5           | 110 ± 90                                      |
|                     | Co–O     | 3.69 ± 0.02         | 6.4 ± 1.6           | 260 ± 100                                     |
| Mn-doped film       | Mn–O     | 1.93 ± 0.01         | 4.4 ± 0.6           | 35 ± 25                                       |
|                     | Mn–Zn    | 2.98 ± 0.02         | 4.6 ± 2.7           | 150 ± 80                                      |
|                     | Mn–Zn    | 3.43 ± 0.01         | 1.5 ± 1.4           | 0 ± 90                                        |

Multiple scattering paths. Table 1 lists the best fits to the data, and figure 2 displays overlaid data and fitted curves. For all films, the measured signals were small due to the low dopant concentration, and the lack of structural order in the Mn-doped film prevented the fitting of a second metal–oxygen shell. Furthermore, long-range disorder in the films also reduced the accuracy of each fit at higher radial distance. The first metal–oxygen shell of both Co- and Mn-doped films is 4, consistent with a substitution for tetrahedral (T$_d$) Zn$^{2+}$ ions in the ZnO structure. Inclusion of the spinels ZnAl$_2$O$_4$ and ZnMn$_2$O$_4$ (a possible contaminant phase [14]) did not significantly improve the fits, though their contribution to the EXAFS cannot be discounted. Antiferromagnetic Co$_3$O$_4$ is another possible contaminant spinel phase, containing Co$^{2+}$ and Co$^{3+}$ on tetrahedral and octahedral sites, respectively. However, no phases other than ZnO were identified in the films, e.g. pure elements or other metal oxides, as confirmed by fitting a range of TM and oxide reference samples (figures 2(b) and (d)).

The near-edge (XANES) region of x-ray absorption spectra contains information about the coordination symmetry and valency of the absorbing atoms. The energy of the absorption edge shifts according to the valency of the absorber, since the binding energy of bound electrons rises as the valency increases. Also, the shape of the absorption edge is responsive to the unfilled local density of states and coordination symmetry of the absorbing element. Figure 3(a) shows that the Mn- and Co-doped films exhibit similar K-edge white line shapes to those previously reported for tetrahedrally coordinated TM-doped ZnO [15, 16].

The valency of the dopant ions can be indicated by comparing their edge positions to those of reference oxides with various metal oxidation states. The edge positions here are defined...
as the energy corresponding to normalized absorption of 0.5 (i.e. half the main absorption edge). Figure 3(b) indicates that Co ions in the film are in 2+ to 3+ oxidation state. By contrast, in figure 3(c) the valency of Mn ions in the Mn-doped film appears to be between 3+ and 4+ [17].

Figure 3(c) also shows that the Mn-doped film has a very different K-edge shape to the reference Mn oxides, indicating a substantial difference in coordination symmetry. In particular,
Figure 3. K-edge XANES of thin film samples and reference powders: (a) solid black line: ZnO powder at the Zn K-edge [9]; red stars: Mn-doped film at the Mn K-edge; blue dots: Co-doped film at the Co K-edge. (b) Co K-edge XANES. Dashed green line: Co foil; red triangles: CoO; blue dots: Co$_3$O$_4$; solid black line: Co-doped film. (c) Mn K-edge XANES. Dashed green line: Mn foil; red squares: MnO; blue dots: Mn$_3$O$_4$; pink triangles: Mn$_2$O$_3$; turquoise diamonds: MnO$_2$; solid black line: Mn-doped film.

The Mn K-edge shows a sharp white line just after the absorption edge, similar to Zn$^{2+}$ in ZnO, but different to the reference oxides in which the Mn site is either octahedral (O$_h$) or mixed O$_h$ and T$_d$. A similarly prominent white line is also produced by Mn(II)acetylacetonate in which Mn is tetrahedrally coordinated to oxygen [18]. Therefore, the XANES supports the EXAFS data in indicating that Mn substitutes for T$_d$ Zn$^{2+}$ in ZnO.

Figure 4 shows the measured L-edge XANES and XMCD of the Co- and Mn-doped films. By contrast to bulk-sensitive K-edge XANES, L-edge measurements are sensitive only to the first few nanometres nearest to the film surface. This is due to the short (∼2–3 nm) escape depth of the excited photoelectrons for electron yield detection [5]. Atomic multiplet calculations were employed to independently determine the electronic configuration and site symmetry of...
Figure 4. Normal incidence L-edge XANES (lower panels) and XMCD (upper panels) at 6 K and corresponding atomic multiplet calculations for (a) Co and (b) Mn dopants. Upper panels: (a) and (b) black line: XMCD at ±5 T; (a) red line: normalized atomic multiplet calculation for $T_d$ Co $d^7$ XMCD; (b) red line: normalized atomic multiplet calculation for $T_d$ Mn $d^4$ XMCD. Lower panels: (a) and (b) XANES at $-5$ T (blue line) and $+5$ T (pink line); black line: average measured XANES; (a) red line: normalized atomic multiplet calculation for Co XANES; (b) red line: normalized atomic multiplet calculation for $T_d$ Mn $d^4$ XANES. The spectra are offset vertically for clarity.

the dopants. The average Co L-edge lineshape closely resembles examples of Co-doped ZnO in the literature [19, 20]. In agreement with these publications, the XANES and XMCD were characteristic of $T_d$ Co $^{2+} d^7$, as shown by the atomic multiplet calculations in figure 4(a). Furthermore, we can clearly exclude $O_h$ Co $^{2+} d^7$ such as in CoO, which shows a distinctly different multiplet structure [21].

The Mn L-edge XANES also shows a distinct multiplet structure. However, in this case the lineshape is not fully reproduced by an atomic multiplet calculation for either Mn $d^5$, $d^4$ or $d^3$ in $T_d$ symmetry. Therefore, in order to determine the valency, the Mn L-edge position in the ZnO:Mn film was compared with a (Ga,Mn)As film measured during the same experimental run [22]. The peak of the XANES is 2.4 eV higher in the ZnO:Mn film than in (Ga,Mn)As, which corresponds to a change of valency of approximately one electron [6, 7]. Since the $d^5$ configuration of Mn in GaAs is well established [1], this indicates that the Mn in the near-surface region of the ZnO:Mn film has a $d^4$ configuration.

Compared with the calculated multiplet spectrum for Mn $d^4$ shown in figure 4(b), both the XANES and the XMCD show additional features at 1–2 eV below the main peak. A broadening
of the Mn L-edge XANES in ZnO:Mn, similar to that reported here but with a lower resolution, was recently reported by Thakur et al [23] and was attributed to the coexistence of d\(^5\), d\(^4\) and d\(^3\) configurations. However, similar spectra have also been reported for a series of compounds with a well-defined Mn\(^{3+}\) valency, e.g. AMnO\(_4\) compounds [24, 25], as well as MnO\(_2\) [17] and MnOOH [26]. In these compounds, the appearance of the low-energy features is ascribed to a lowering of the octahedral symmetry of the d\(^4\) ion by Jahn–Teller distortion. Also, Jahn–Teller distortion of T\(_d\) V d\(^3\) in Zn\(_{1-x}\)V\(_x\)O and T\(_d\) Cr d\(^4\) in Zn\(_{1-x}\)Cr\(_x\)Te were recently reported, resulting in C\(_{3v}\) and D\(_{2d}\) symmetry, respectively [27, 28]. The Jahn–Teller mechanism should similarly lead to a lowering of the T\(_d\) symmetry in ZnO:Mn \(^{3+}\), and this is the most likely explanation for the low-energy features in the multiplet structure.

The field dependence of the XMCD was investigated to determine the nature of the magnetic coupling between the dopant ions. The XMCD, which is proportional to the net magnetization, increases steadily as a function of the magnetic field at the measurement temperature of 6 K, indicating paramagnetic behaviour. In figure 5, the XMCD signals are compared with Brillouin functions calculated for Mn d\(^4\) with total angular momentum \(J = 2\) and Landé g-factor \(g = 2\), and Co d\(^7\) with \(J = 3/2\) and \(g = 2\) (i.e. neglecting the orbital moment, which is found to be much smaller than the spin moment from applying sum rules to the XMCD spectra). There is very good agreement between the measured data and the Brillouin function calculations, showing that the Mn- and Co-doped films are paramagnetic. When the XMCD curves at different fields are normalized to the L\(_3\) peak, the spectra overlay completely, indicating a single magnetic environment for both Co and Mn, and thereby demonstrating film homogeneity [20, 29].

### 4. Conclusions

XRD showed that the sol-gel-synthesized Co- and Mn-doped ZnO films consist principally of the c-axis orientated wurtzite ZnO. Detailed analysis of x-ray absorption spectra, including fitting of EXAFS data, comparison of K-edge XANES with reference oxide spectra and atomic multiplet analysis of L-edge XANES and XMCD spectra, indicate that the Co and Mn dopants are incorporated in fourfold coordinated sites. The Co (Mn) oxidation state is found to be...
Evidence for Jahn–Teller distortion of the $\text{Mn}^{3+}$ ion is also observed. Dopant L-edge XMCD for both Co- and Mn-doped ZnO films follow a Brillouin-like dependence on the applied magnetic field indicating paramagnetism. Similar paramagnetic-like behaviour of the XMCD in ZnO:Co films [20, 30] as well as ZnO:Cu films [31] has been reported elsewhere, although in each of these cases it was reported that bulk magnetometry measurements yielded a ferromagnetic signal at room temperature. While a small room temperature ferromagnetic signal was also observed for the present samples (from vibrating sample magnetometry), this could not be definitively ascribed to the ZnO film, with substrate contamination being a more likely source of the signal. It is striking that the technique, which is most selectively sensitive to the magnetic order of the doped films, reveals only a paramagnetic response. This work therefore casts further doubt on the existence of ferromagnetism in TM-doped ZnO, and demonstrates the importance of making a careful study of all possible phases, especially those below the detectable limit for XRD, as well as extrinsic sources of contamination. These insights were made possible using synchrotron-based x-ray absorption and magnetometry techniques that are highly sensitive and selective compared with laboratory-based structural and magnetic measurements.

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