Defect ferromagnetism in ZnO and SnO2 induced by non-magnetic dopants

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Defect ferromagnetism in SnO$_2$:Zn$^{2+}$ hierarchical nanostructures: correlation between structural, electronic and magnetic properties

This chapter reports on Sn$_{1-x}$Zn$_x$O$_2$ (x ≤ 0.10) hierarchical architectures with nanosphere, nanocube, and nanoflower morphologies synthesized by a solvothermal route. A room temperature ferromagnetic and paramagnetic response was observed for all compositions with a maximum for x=0.04. The ferromagnetic behaviour was found to correlate with the presence of zinc as a substitutional defect and with a low oxygen vacancy concentration in the samples. The morphology of the nanostructures varied with zinc concentration. The strongest ferromagnetic response came from nanostructures with well-formed shapes, having nanoneedles on their surfaces. These nanoneedles consist of (110) and (101) planes, which are important in stabilizing the ferromagnetic defects. At higher zinc concentration the nanostructures become eroded and agglomerated; this morphology change was accompanied with a strong decrease in their ferromagnetic response. The observed trends are explained in the light of recent computational studies that discuss the relative stability of ferromagnetic defects on various surfaces and the role of oxygen vacancies in degrading ferromagnetism via an increase in free electron concentration.

# The results presented in this chapter are summarized in a manuscript ready for submission:
5.1 Introduction

Stannic oxide (SnO$_2$) is a wide band gap semiconductor that exhibits both relatively high electrical conductivity and insulator like transparency in the visible range. Such properties of SnO$_2$ in combination with other materials enable wide usage in optical and solar cell applications$^{1,2}$. The reports of room temperature ferromagnetism (FM) in both pure$^3$ and non-magnetically doped SnO$_2$ hold promise for increased functionalities of this system$^{4-13}$. FM in such systems is explained in general as a consequence of various defect-induced local structures that lead to modifications of the local charge density and the consequent polarization of the spin bands. Despite the general consensus on the role of defects there is little unanimity on the specific defects that are important and on the mechanism whereby they are stabilized. These defects include vacancies, Sn vacancies and cation (dopant) substitution on Sn sites. However it is also known that such defects have different formation energies that are in general very sensitive to the local atomic neighbourhood and to the ambient conditions during synthesis. Consequently the stability of these moment-supporting defects varies with dopant concentrations and their specific location in the lattice structure. In the work reported in this chapter we studied the magnetic and morphological aspects of Zn-doped SnO$_2$; we discuss the observed room temperature ferromagnetism in terms of stabilization of relevant defects.

Initial research efforts in this field were focused on magnetic transition metal (TM) doped SnO$_2$ nanoparticles and thin films (Co, Cr, Mn, Fe, Ni and V)$^{14-16}$ that display ferromagnetism. To avoid magnetic metal clusters or secondary phases of SnO$_2$ doped with nonmagnetic (NM) elements (e.g. Cu and Zn)$^{4-6}$, alkali metals (Li and K)$^{7-9}$, alkali earth metals (Mg)$^5$, non-metals (C and N)$^{10,11}$, and poor metals (In and Ga)$^{12,13}$ have also been studied and the FM has been reported. Density functional studies$^{17}$ have shown that Sn vacancies (V$_{Sn}$) are responsible for the observed giant magnetic moment (GMM) of TM-doped SnO$_2$. Other computational studies$^{18}$ describe surface magnetism induced in a C-doped (001) surface and the incorporation of Li$^{+1}$ at (001) surface sites$^{19}$ of SnO$_2$. Surface magnetism in Cu-doped (110) surfaces in SnO$_2$ thin films has also been predicted$^{20}$. The role of divalent zinc as a substituent for Sn$^{4+}$ is particularly interesting due to the closeness in their respective ionic sizes and the difference in their valence. Doping of Zn in SnO$_2$ has been shown to induce magnetism in nanoscale systems$^6,21$ while computational studies performed on the bulk SnO$_2$ system with Zn doping relate this magnetism
to the native defect of tin vacancies\textsuperscript{22, 23}. The other prevalent defects in this system, namely oxygen vacancies ($V_O$) are known to impair FM. It has been reported\textsuperscript{24} that divalent Zn\textsuperscript{2+} and Cd\textsuperscript{2+} ions substituting for Sn\textsuperscript{4+} introduce holes in the 2$p$ orbitals of the O atoms; the induced magnetic moment comes mainly from the O 2$p$ orbitals and is largest at the first O atom neighbouring the dopant. Hence electron deficiency at the oxygen site, whether originating from the $V_{Sn}$ or from replacement of Sn\textsuperscript{4+} by Zn\textsuperscript{2+}, leads to holes in the O 2$p$ band and to the possible polarization of this band. The contribution of the $V_{Sn}$ to the moment itself is usually very small.

The incorporation of zinc in SnO$_2$ and the stability of other common defects is however sensitive to the specific surface where these defects formed. Recently Pushpa \textit{et al.}\textsuperscript{25} have studied the formation energies and moments for various defects in the bulk, at the surface and in sub-surface layers, in both Sn-rich and O-rich conditions. In general it is easier to form both Sn and O vacancies at surfaces than in the bulk and the (001) surface is preferred to the (110) surface. They show that while the $V_{Sn}$ defect is magnetic for both bulk and (110) surfaces, its formation energy remains very high even at the surface. The oxygen vacancy on the other hand has no magnetic moment in the bulk or on either of the two surfaces studied. The Zn substitutional defect ($Zn_{Sn}$) possesses a small moment of $\sim$0-0.11 $\mu_B$/Zn but generates a significant moment per cell (2$\mu_B$/cell). The formation energy on the (001) surfaces is about half that of the bulk, while on the (110) surfaces it is close to that of the bulk. Interestingly, the Zn atom on the (110) surface does not contribute to the induced moment directly. The moment arises from the nearest neighbour bridging oxygen and minimally from the in-plane oxygen or the Sn atom. It is further understood that while the moment arises from the polarization of the partially filled oxygen bands, the occurrence of ferromagnetism or antiferromagnetism (AFM) in these bands depends on the separation between the holes on oxygen atoms surrounding the $V_{Sn}$ defect.

Alongside these studies of the electronic and FM/AFM properties, there are various reports of unique morphologies in SnO$_2$-based systems that display hierarchical nanostructures with nanorods, nanosheets and nanoflowers at different scales, often as a function of stoichiometry\textsuperscript{26-28}. The formation of these nanostructures is related to differences in the growth rates of various crystallographic planes in the presence of these defects, \textit{e.g.} oxygen vacancies, substitutional atoms \textit{etc}. Several previous reports\textsuperscript{26, 27, 29-34} have demonstrated that the morphologies and properties of SnO$_2$ can be modified by Zn doping since incorporation of zinc into the SnO$_2$ lattice modifies the local structure and the growth rate of different crystallographic planes. In
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particular Zn$^{2+}$ ions in the SnO$_2$ lattice inhibit the growth along the [110] direction, promoting the anisotropic growth of nanorods. Hence the morphological and electronic properties become interrelated in this system since the formation energies of the moment supporting defects (e.g. Sn vacancies) are different for different such surfaces or planes. While this aspect may not be particularly important for bulk systems, it assumes a different significance for nanostructured materials due to their large surface to volume ratios; there preferential growth of a certain surface affects the magnitude of the magnetic moment.

In the light of the preceding discussion on the role of specific planes in lowering the formation energy of defects and stabilizing ferromagnetism, we prepared nanoparticles of Zn-doped SnO$_2$. A solvothermal synthesis route was adopted that resulted in hierarchical nano-architectures with well-defined planar surface structures that change with Zn concentration. Alongside the structural changes the magnetic behaviour also changes and the study reported in this chapter attempts to relate and understand the observed variations in structure, morphology and magnetic behaviour.

5.2 Experimental details

Sn$_{1-x}$Zn$_x$O$_2$ nanoparticles with varying Zn concentration (x=0, 0.02, 0.04, 0.06, 0.10) were synthesized by a simple solvothermal method at room temperature. All chemicals were of analytical grade and used without further purification. 0.1 M of SnCl$_4$·5H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O were separately dissolved in a mixture of ethanol and deionized (DI) water with a 1:1 volume proportion. Then a ethanol-DI water solution containing 2.4 g NaOH was slowly dropped into the mixture of the two solutions under rigorous stirring. After 30 minute, the solution of the resultant mixture (pH value ~ 11) was transferred into a 100 mL Teflon-lined stainless steel autoclave and kept at 160 °C for 22 h. The resulting precipitates were centrifugally separated and washed several times with ethanol and DI water. Finally, the products were dried in air at 80 °C for several hours. NaOH is a very favourable additive for the growth of 1D SnO$_2$ nanostructures, with [001] direction as the growth axis and (110) as the family of enclosing facets$^{35}$. Higher pH used in the synthesis accelerates the nucleation rate, which results both in a higher nuclei concentration and in higher growth rates of nanoparticles. As discussed in detail in reference 26, when Zn$^{2+}$ ions are introduced into the solution, some Sn$^{2+}$ ions are substituted, forming
compound nuclei under the solvothermal conditions. Later some of these nuclei grow into nanosheet structures through aggregation\textsuperscript{36} and Ostwald ripening\textsuperscript{37} under the influence of Zn\textsuperscript{2+}. Finally, the nanosheets aggregate to reduce the surface area and the associated surface energy. All experimental details are described in Chapter 2: X-ray diffraction (XRD) with Cu Kα radiation (λ= 1.5405 Å) was used for the structural analysis of the samples; the morphology and microstructure of the samples were investigated using Field Emission Scanning Electron Microscopy (FESEM) equipped with energy-dispersive X-ray spectroscopy (EDX) and High Resolution Transmission Electron Microscopy (HRTEM); X-ray photoelectron spectroscopy (XPS) was carried out using an SSX-100 (Surface Science Instruments) spectrometer; magnetic characterization of the samples was performed with the help of a Quantum Design MPMS-XL7 SQUID magnetometer.

5.3 Results and discussion

5.3.1 Structural analysis

Figure 5.1 (a) presents the X-ray diffraction (XRD) data of the undoped and the Zn-doped SnO\textsubscript{2} nanoparticles. All the diffraction peaks in the pattern correspond to the tetragonal rutile structure of polycrystalline SnO\textsubscript{2} (JCPDS File No. 41-1445 Å). No phase corresponding to zinc or other zinc compounds was observed, indicating that zinc gets incorporated into the tin oxide lattice. These XRD patterns were refined with the help of the X’Pert High Score Plus software and by the Rietveld refinement technique\textsuperscript{38}. A typical XRD pattern along with the refinement is shown in Figure 5.1 (b) for the Sn\textsubscript{0.96}Zn\textsubscript{0.04}O\textsubscript{2} sample. It can be clearly seen that the experimental X-ray peaks accurately match the software generated peaks. Using the XRD data, the cell parameters $a$, and $c$ were calculated for different doping concentrations ($x$), and their average values are plotted in Figure 5.2 (a) and (b) respectively. The trend of the calculated values clearly indicates an increase in the values of lattice parameters $a$ and $c$ with increasing Zn concentration up to $x$=0.04. Thereafter both $a$ and $c$ decrease for $x$>0.04 up to the highest concentration studied, namely $x$=0.10.
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Figure 5.1 (a). XRD patterns of Sn$_{1-x}$Zn$_x$O$_2$ with $x$ varying between 0 and 0.10. Inset: detail of the (110) peak, which shifts with Zn addition. (b). Rietveld refinement of XRD pattern for the $x$=0.04 composition.

Figure 5.2 Variation of (a) lattice parameter “c” and (b) lattice parameter “a” determined from XRD as function of Zn concentration ($x$) in Sn$_{1-x}$Zn$_x$O$_2$.

The increase in the lattice constant is consistent with Sn$^{4+}$ ions being replaced by Zn$^{2+}$ since the radius of Zn$^{2+}$ (0.74 Å) is larger than that of Sn$^{4+}$ (0.69 Å). This increase in lattice parameters is therefore a clear indication that between $x$=0.00 and $x$=0.04 nominal concentration, Zn substitutes for Sn in the SnO$_2$ lattice (Zn$_{Sn}$). However the observed decrease in the lattice constant at higher Zn concentration suggests that there the effect on the cell volume is dominated by the development of oxygen vacancies whose presence is required for charge compensation.
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when Zn$^{2+}$ substitutes for Sn$^{4+}$. At these higher concentrations there is also a possibility that the added zinc atoms may enter vacant O sites. In agreement with this hypothesis DFT calculations indicate that in Sn-rich conditions the energies of formation of the Zn$_{Sn}$ and Zn$_O$ defects are very close. Such behaviour would also lead to a cell volume reduction since the size of Zn$^{2+}$ is much smaller than that of O$^{2−}$ (1.4 Å). We also note that with increasing Zn concentration the diffraction peaks decrease in intensity and tend to become broader as shown in the inset of Figure 5.1 (a). The changes in intensity and full width at half maximum (FWHM) indicate that the incorporation of Zn dopants results in the deterioration of crystallinity and the decrease of grain size in Sn$_{1-x}$Zn$_x$O$_2$ samples. The average grain size was estimated using the FWHM of (110) and (101) peaks based on Scherrer’s equation. As the Zn concentration in in Sn$_{1-x}$Zn$_x$O$_2$ increases from x=0.02 to x=0.10, the average grain size decreases from 80.0±2.1nm to 15.0±2.1nm. This aspect will be discussed further in the context of the morphological studies on these particles.

Energy dispersive X-ray spectroscopy (EDS) was carried out to determine the elemental composition and to check for the presence of any unwanted magnetic impurity within the instrumental detection limit of 1%. The analysis confirms that there is no detectable trace of magnetic impurities in the compounds. The results are shown in Figure 5.3. The elemental analysis corroborates the presence of Zn, Sn and O; note that there are also the Si and C signals coming from the sample holder with conductive tape.

5.3.2 Morphology and structure of Zn-doped SnO$_2$ hierarchical architectures

The morphology of the Zn-doped SnO$_2$ with different Zn content was studied by FESEM, EDS and TEM. Figure 5.4 (a-d) shows FESEM images for Sn$_{1-x}$Zn$_x$O$_2$ samples with x=0.00, 0.04, 0.06 and 0.10 and (I, II) represent the corresponding higher magnification micrographs.

These images illustrate the changes in morphology observed for different Zn concentration. Figure 5.4 (a) shows spherical aggregated nanoparticles of undoped SnO$_2$ (x=0.00) with sizes in the range 50–200 nm. Figure 5.4(b) reveals that with the addition of Zn (Sn$_{0.96}$Zn$_{0.04}$O$_2$) the aggregated undoped nanospheres grow into micron size cubes, spheres and some into eroded
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Figure 5.3 EDS of (a) undoped, (b) Sn$_{0.96}$Zn$_{0.04}$O$_2$ and (c) Sn$_{0.90}$Zn$_{0.10}$O$_2$ nanoparticles.

spheres. Some of the surfaces of the Zn doped particles are covered with fine needle-like growth, while a few of the nanospheres acquired a flowerlike morphology. Figure 5.4(c) and (d) present images for the Sn$_{1-x}$Zn$_x$O$_2$ with $x=0.06$ and $x=0.10$ respectively. It can be seen that with increasing Zn concentration the previously spherical and cubical particles become eroded and acquire different shapes of hierarchical structures. These include a mixture of hemi and hollow spheres, and an elongated chain of flower-type structure. We also observed that for higher zinc concentration these micron size structures became interconnected by nano-needles on their surfaces. For $x=0.10$ one sees a clear erosion of the individual spherical and/or
Figure 5.4 FESEM micrographs of Zn$_x$Sn$_{1-x}$O$_2$ nanoparticles with (a) $x=0.00$, (b) $x=0.04$, (c) $x=0.06$ and (d) $x=0.10$, where I and II represent the corresponding higher magnification micrographs.
cubical structures, which now agglomerate to form a bundle of nanoflowers or different shapes, with nano-needles on their surfaces. For further analysis of the surface nanoneedles, TEM and HRTEM were performed on a Sn_{1-x}Zn_xO_2 sample with x=0.04. Figure 5.5 (a) presents an image of this sample where micron sized particles with both cubical and spherical shapes can be seen. High resolution TEM images in Figure 5.5 (b-e) clearly show that these micron size particles are covered with outward growing nanoneedles, nanorods and nanostructures extending from the surface. The length of these nanoneedles is in the range 10–100 nm (Figures 5.5 (d), (e)), and connecting nanorods measure about 85 nm x 280 nm (Figure 5.5 (d)). Figures 5.5 (f) and 5.5 (g) show HRTEM micrographs of long and small nanoneedles. The two groups of crystallographic planes marked in the images have interplanar distances of 0.35 nm and 0.26 nm respectively. These separations match well with the (110) and (101) planes of rutile SnO_2. It is known that in SnO_2 the (110) surface has the lowest surface energy followed by the (100), (101) and (001) surfaces. Nanocrystals have a high surface energy and tend to aggregate to decrease the surface energy. It is understood that during the initial stage of the reaction process, oxidation of Sn^{4+} produces SnO_2 spherical nanoparticles with a diameter of 50–200 nm. Then these nanoparticles aggregate into solid cubes with needles on the surface for the minimization of overall system energy. It should be noted that these solid cubes and spheres are all composed of nanocrystalline particles, as shown in Figure 5.5 (b). A similar behaviour has been observed and demonstrated in the preparation of other hollow structures, such as hollow Cu_2O cubes and hollow TiO_2 spheres. Furthermore, in the absence of Zn^{2+} ions, a similar morphology was not obtained and pure SnO_2 (Figure 5.5 ((a)) shows no evidence for nanoneedle-like growth or interconnecting nanorods. While similar nanostructures have been reported in pure SnO_2 nanoparticles, their development in un-doped SnO_2 appears connected to the presence of Sn^{2+} ions. In the case of Zn-doped SnO_2, the role of Zn^{2+} as a structure directing agent has been reported and is confirmed by our results. The substitution of Zn^{2+} for Sn^{4+} leads to doubly charged oxygen vacancies, V_O^{2+}. As a consequence the charge density and surface energy of various crystal faces is changed, leading to a large polarity in the growth of Zn-doped SnO_2, which in turn yields different growth rates for different surfaces. As already discussed, the average crystallite size estimated by Scherrer’s formula decreases with the addition of Zn,
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Figure 5.5 TEM (a, b, c, d, and e) and HRTEM (f and g) images of Zn$_x$Sn$_{1-x}$O$_2$ with $x=0.04$. HRTEM focuses on the nanoneedles extending from the nanoparticle surfaces in Figure 5.5 (a-e). The (110) and (101) planes are visible.

suggesting that the zinc dopant plays an active role in reducing the average crystallite size. Supposedly the addition of Zn can promote a high rate of nucleation during the SnO$_2$ crystallization process. After nucleation most of the Zn$^{2+}$ ions will segregate to surface/interface sites because of the abundant surface area available. When these ions occupy the surface sites of SnO$_2$ nanocrystals, they most likely inhibit the formation of necks between particles and the coalescence of tiny SnO$_2$ crystals into larger particles (microcubes and microspheres).

Thus our study helps to establish some important differences between morphologies of low and high zinc concentration nanoparticle systems. Whereas the former have well-developed isolated structures that exhibit needle like growth on the surfaces, the latter exhibit small grain sizes for individual particles with erosion of shapes and agglomeration of the particles.
5.3.3 X-ray photoelectron spectroscopy (XPS) analysis

The chemical composition of the hierarchical nanostructures was studied by XPS. Figure 5.6 (a), (b) and (c) display the spectra of the Sn 3d, Zn 2p and O 1s core level regions for undoped SnO$_2$, and for Zn$_x$Sn$_{1-x}$O$_2$ with $x=0.04$ and $x=0.10$.

**Figure 5.6** XPS spectra of the (a) Sn 3d, (b) O 1s and (c) Zn 2p core level regions for Zn$_x$Sn$_{1-x}$O$_2$ with $x=0.00$, 0.04 and 0.10.

The undoped SnO$_2$ spectrum shows Sn 3d$_{5/2}$ and 3d$_{3/2}$ peaks of the Sn$^{4+}$ ions at binding energies of 485.9 and 495.3 eV respectively. We note that Zn doping decreases the binding energy of the Sn 3d peaks as compared with the undoped SnO$_2$ sample by 1.6 eV. This shift can be attributed to the presence of an increasing number of oxygen vacancies at higher Zn content$^{31,44,45}$. Figure 5.6 (b) displays the O 1s spectra for undoped, $x=0.04$ and $x=0.10$ Zn doped SnO$_2$ samples. The main peak centred at 531.2 eV for $x=0.00$, at 529.9 eV for $x=0.04$ and at 528.6 eV for $x=0.10$ is attributed to the coordination of oxygen in Sn–O–Sn, while the shoulder corresponds to Sn–O–Zn bonds$^{31,39}$.

Also here a chemical shift towards lower binding energy as a function of Zn-doping is observed and can be attributed to the increasing number of V$_O$, analogously to the Sn 3d chemical shift. Figure 5.6 (c) displays the Zn 2p core level region where the two spin-orbit-split peaks appear at binding energies of 1021.1 eV and 1044.10 eV$^{46}$, confirming that Zn atoms have been incorporated into the Sn lattice and form Zn–O bonds.
5.3.4 Magnetic analysis

Magnetization measurements M(H) were carried out at room temperature for all samples and for selected compositions at 5 or 50 K. Magnetization versus temperature data were also recorded for Zn$_x$Sn$_{1-x}$O$_2$ with x=0.04. Figure 5.7 shows the field dependence of the magnetization M(H) for all the samples studied. Pure SnO$_2$ was diamagnetic at room temperature while at 5 K it showed paramagnetic behaviour, i.e. a linear dependence of the magnetization on the applied field. It can be seen that the magnetic moment at high fields is maximum for x=0.04 and declines strongly for lower and higher Zn content. All Zn-doped SnO$_2$ samples show the presence of two contributions. Firstly there is a non-linear or ferromagnetic component with a non-zero remanence and hysteresis at room temperature. The x=0.04 (inset Figure 5.7) and 0.06 compositions were also measured at low temperature and showed a strong increase in both the remanence and hysteresis. The second component of the magnetization is, as evident from Figure 5.7, a linearly increasing or paramagnetic component.

A comparison of both components for various compositions will be discussed later. The magnetization data for the x=0.04 composition as a function of temperature for an applied field of 1000 Oe is shown in Figure 5.8, while the inset shows the inverse of magnetization versus temperature. It is apparent from the curvature of the 1/M versus T that the data does not show a good Curie-Weiss behaviour. This is of course not surprising, since the full magnetization includes a ferromagnetic component in addition to the paramagnetic part.

To separate out the two components we fitted the higher field data of the magnetization versus field (Figure 5.7) to the expression M=M$_0$+cH (where c is a constant) and from the linear fit the value of M$_0$ was extracted, which will be referred to as the ferromagnetic component. The procedure is illustrated in Figure 5.9 (a). The values of c, the fitting constant representing the paramagnetic susceptibility, were obtained from the fits at T=50 and 300 K respectively. The ratio was found to be 5.2, which is close to the expected value of 6 for a purely paramagnetic behaviour, $\chi \sim 1/T$.

The ferromagnetic component M$_0$ for each composition was obtained by the above procedure and then subtracted from the full moment measured at H=10 kOe. The resultant value for each composition is referred to as the paramagnetic component.
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Figure 5.7 Room temperature magnetization (M) versus magnetic field (H) of Sn$_{1-x}$Zn$_x$O$_2$ with $x=0.00$, 0.02, 0.04, 0.06 and 0.10. Inset M vs H at 50 K of Sn$_{1-x}$Zn$_x$O$_2$ with $x=0.04$.

Figure 5.8 Magnetization versus temperature for Sn$_{1-x}$Zn$_x$O$_2$ with $x=0.04$ with an applied field of 1000 Oe. The inset shows 1/M vs. temperature, which deviates from a straight line.

The same procedure was also followed for the analysis of the data at lower temperatures, for Sn$_{1-x}$Zn$_x$O$_2$ with $x=0.04$ and $x=0.06$. The variation of both the magnetic components is shown as a function of the composition in the main part of Figure 5.9 (b). The inset shows the same two
components with the magnetization in Bohr magnetons per zinc atom. Here the number of zinc atoms corresponds to the nominal concentration. We can see that the ferromagnetic moment per zinc atom is a maximum at $x=0.04$ and somewhat smaller for the $x=0.02$, while it falls sharply at $x=0.06$. We note that for $x=0.02$ and $0.04$ the lattice constant shows an expansion compared to $x=0.00$, which indicates that zinc predominantly substitutes at Sn sites. The strong decline of the ferromagnetic moment/zinc atom for $x=0.06$ coincides with the contraction of the lattice constant as shown in the XRD data.

Similarly the paramagnetic component/zinc atom (inset of Figure 5.9 (b) is maximum at $x=0.04$ and decreases very little for $x=0.06$. However this contribution drops very strongly for $\text{Sn}_{1-x}\text{Zn}_x\text{O}_2$ with both $x=0.02$ and $x=0.10$. This suggests that while the zinc dopants do not lead to a large ferromagnetic component for $x > 0.04$, they are still able to contribute strongly to the paramagnetic part for $x=0.06$. Consistent with the earlier discussion of the structural and electronic effects (see discussion of XPS data) it is possible that the observed variation of the ferromagnetic moment per zinc atom reflects a competing effect of two contributions, namely zinc dopants as hole contributors and stabilizers of Sn vacancies on the one hand and oxygen vacancies as electron donors on the other. For $x=0.02$ and $0.04$ the zinc atoms substitute for Sn but the number of oxygen vacancies is relatively small, leading to a larger ferromagnetic component. For higher Zn content it is possible that in addition to increasing the number of O vacancies, zinc occupies some sites other than those of Sn, e.g. O sites. Both features are expected to lead to a decline of the ferromagnetic behaviour. However the paramagnetic part can still be contributed to as will be discussed next. There may be two different sources for this paramagnetic part. Firstly the magnetic moment developed at sufficiently isolated defect sites ($\text{Zn}_{\text{Sn}}$) will not lead to a stabilization of the FM\textsuperscript{17} but the paramagnetic contribution may still exist. Secondly we note that singly ionized oxygen vacancies can also yield a paramagnetic contribution. At room temperature all neutral $\text{V}_\text{O}$ centres (an oxygen vacancy with two trapped electrons) are dissociated into singly ionized oxygen vacancy $\text{V}_\text{O}^+$ (an oxygen vacancy with a single trapped electron) and a free electron. These singly charged oxygen vacancies have been reported to be paramagnetic\textsuperscript{47}. The decrease in this paramagnetic contribution at higher zinc concentration $x=0.10$ is then attributable to the recombination of O 2p holes with the trapped electron of the $\text{V}_\text{O}^+$ converting it\textsuperscript{47, 48} into a nonmagnetic $\text{V}_\text{O}^{2+}$. We believe this is the most plausible explanation for the variation of the paramagnetic moment with zinc concentration.
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5.4 Conclusions

Our measurements have shown, as have earlier studies$^{6, 21}$, that incorporation of zinc in SnO$_2$ nanoparticles enhances the ferromagnetic response very significantly but in a limited range of zinc concentrations. Structural and XPS studies confirm that the enhancement is strong in the region where zinc is incorporated substitutionally and the oxygen vacancy concentration is relatively small. This is understood in a picture where zinc substituting for Sn acts as a hole dopant for the O 2$p$ bands, while oxygen vacancies counteract the effect by introducing electrons and reducing the hole concentration thereby degrading the ferromagnetic response. There is a pronounced paramagnetic response, which we understand as originating in the singly charged oxygen vacancies and possibly also from magnetic defects that are too far apart to stabilize ferromagnetism. We find that the introduction of zinc leads to marked changes in the morphology of the nanoparticles. In particular, we identify that for the more strongly ferromagnetic compositions the nanoparticles have regular shaped structures with nanoneedles on their surfaces where the (110) and (101) planes are present. This is particularly significant in

Figure 5.9 (a) Magnetization (M) versus magnetic field (H) of Sn$_{1-x}$Zn$_x$O$_2$ with x=0.04 at 300 K and 5 K and linear fit at high fields, (See text for details). (b) The variation of the ferromagnetic, M(FM), and paramagnetic, M(PM), components extracted from plots like Figure 5.9 (Right panel) (as described in the text) shown as functions of the Zn composition (x). The inset shows the same two components with the magnetization in Bohr magnetons per Zn atom.
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the sense that calculations$^{21}$ have shown that ferromagnetic defects ($V_{Sn}$) are energetically particularly favoured on these surfaces. Hence there appears to be a correlation between the morphological structure and ferromagnetic behaviour via the anisotropic growth of nanostructures with surfaces that stabilize ferromagnetic defects. Thus ferromagnetism of the defects formed in Zn-doped SnO$_2$ is a synthesis of three factors, namely, stabilization of $V_{Sn}$ and Zn$_{Sn}$ defects; oxygen vacancies required for charge compensation and finally morphological variations that in turn affect both preceding factors by controlling the stabilization energies of various defects.

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