Solvent Dependent Shape and Magnetic Properties of Doped ZnO Nanostructures**

By Guylhaine Clavel, Marc-Georg Willinger, David Zitoun,* and Nicola Pinna*

This study reports on a new solution phase synthesis leading to cobalt and manganese doped ZnO which have been theoretically predicted ferromagnetic at room temperature. The solvothermal synthesis involving the reaction of zinc and cobalt acetate or manganese oleate with benzyl alcohol leads to pure inorganic nanoparticles that are diluted magnetic semiconductors. The addition of an inert solvent, that is used in order to control the amount of benzyl alcohol, drastically influences the particles morphology and strongly affects the magnetic behaviors. Cobalt doped particles are paramagnetic or ferromagnetic depending on the synthesis conditions. In order to exclude the formation of secondary phases and/or metal clusters and to understand the role of the solvent on the magnetic properties, the local structure of Co^{2+} and Mn^{2+} in the wurtzite ZnO matrix were characterized by XRD, UV-visible diffuse reflectance and electron paramagnetic resonance.

1. Introduction

Zinc oxide (ZnO) has been the subject of numerous studies in the past ten years for its optical properties. The material is already used for the fabrication of highly efficient blue LEDs.[1] Doping has also been performed on ZnO in order to tune the emission from the bandgap and from the defects. These studies have certainly found some echo in another scientific area, namely the study of diluted magnetic semiconductors (DMS). Obviously, the use of carrier spin, in addition to the charge, appears very promising for the emergence of polarized emitters.[2,3] A key requirement for the use of spin based electronic devices (spintronic) is the persistence of ferromagnetism above room temperature. Early studies on manganese doped ZnO devices (spintronic) is the persistence of ferromagnetism above room temperature. The high-temperature synthesis process was shown to be the origin of the magnetic behavior in the case of a ZnO/MnO system grown by high temperature solid state reaction.[5] Consequently, the main point of any new study relies on the exclusion of any secondary phase as origin for ferromagnetism.

The fundamental origin of the observed magnetic behavior has attracted much attention since 2000. In an extremely quoted paper, T. Dietl et al. reported a theoretical study on the Curie temperature of ferromagnetic DMS.[2] Interestingly, the experimental study of manganese doped zinc telluride supported the calculations and room temperature ferromagnetism was predicted for p-type manganese doped ZnO (and n-type cobalt doped ZnO).

The revival of this already old field mainly occurs due to the assumption that room temperature ferromagnetism is indeed promoted by the semiconductor charge carriers, based on the so-called Zener model adapted to DMS. However, many of the claims of high-temperature ferromagnetism in DMS systems are controversial.[4] The high temperature synthesis process may explain the tendency of these materials to phase-separate into a ZnO matrix with transition metal inclusions.[2] The semiconducting properties would then originate from the matrix and the magnetic properties from the clusters. In addition, the exact origin of the observed magnetic behavior in these systems depends on the dopant/matrix system and the carrier concentration and thus on synthetic conditions. For example, it was shown that a secondary phase was the origin of the magnetic behavior in the case of a ZnO/MnO system grown by high temperature solid state reaction.[5] Consequently, the main point of any new study relies on the exclusion of any secondary phase as origin for ferromagnetism.

Mn doped ZnO nanostructures from physical routes have been widely studied as thin films,[6-8] nanorods,[9] or nanowires.[10-13] Similar studies have been carried out on Co doped ZnO with thin films,[14-16] nanorods,[17,18] and nanowires.[10,19,20] One-dimensional systems are particularly interesting for the study of DMS. The morphology offers a wide range of characterizations combined with a high potential for technological applications, as was shown for room temperature ultra-violet lasing.[15]

Two previous papers reported on the synthesis and characterization of Mn and Co doped ZnO nanowires synthesized by a
surfactant assisted route.\cite{21,22} The metal organic precursors were reacted in triocetylamine between 280–310 °C. However, the amine is able to reduce metals at high temperature. Thus, the use of another solvent was needed in order to avoid any possible reduction of the magnetic dopants.

Moreover, solvent assisted synthesis and especially the “benzyl alcohol route” has several advantages over surfactant based routes.\cite{23–25} It allows a good control of the crystal growth without the use of any additional ligands or templates. The final product is then exclusively inorganic and has a clean surface. In fact, its surface can be easily accessed in order to perform reactions (e.g., catalysis or gas sensing)\cite{26,27} and it can be functionalized in order to redisperse the particles in different kinds of solvents.\cite{28,29}

Few reports exist on the synthesis of zinc oxide in alcoholic media and in the majority of these cases, either surfactants are used to control the morphology\cite{30,31} or basic conditions are needed to accomplish hydrolysis of the zinc precursor.\cite{32–36} To the authors best knowledge, only two different studies involve the syntheses in pure alcohol\cite{37,38} and the possibility of doping zinc oxide by this approach has not been explored so far.

Here, we report on the synthesis and magnetic characterization of cobalt and manganese doped zinc oxide nanoparticles with different morphology grown by solvent assisted synthesis. The solution route allows the synthesis of gram-scale quantities of homogeneous nanostructures. This is an important prerequisite for a in depth analysis and macroscopic characterization of the obtained material. This synthetic method also enables the incorporation of several transition metal dopants into the ZnO nanoparticles, such as Mn, Fe and Co. However, we limit this report to the manganese and cobalt-doped systems. We shall show that the doped samples present homogeneous doping precluding clustering and transition metal reduction. Furthermore, the observed magnetic behavior is strongly dependent on the solvents used for synthesis.

2. Results and Discussion

2.1. Structural and Morphological Characterization

This study focuses on the role of solvent on the morphology and magnetic properties of the obtained nanostructures. The nanoparticles were synthesized by reacting zinc acetate and a dopant precursor (cobalt acetate or manganese oleate) with different anisole/benzyl alcohol proportions at moderate temperature (Table 1). Depending on the nature of dopant precursor used, the synthesized product is a green (cobalt) or yellow (manganese) powder.

Figure 1 shows the XRD patterns of the ZnO nanoparticles doped with cobalt (A) and manganese (B). They are plotted in logarithmic scale in order to enhance the signal from any impurity. The obtained XRD pattern is in agreement with the zincite structure. No additional reflections are observed even for the particles including the largest amount of dopant indicating that there are no additional crystalline structures present in the samples. In all cases, wurtzite is the only crystalline phase. The lattice constant does not show any significant shift, certainly resulting from the close values of ionic radii in the case of zinc and cobalt (Zn$^{2+}$ – 0.60 Å, Co$^{2+}$ – 0.58 Å). A shift is supposed to occur only for manganese doping (Mn$^{2+}$ – 0.66 Å). Nevertheless, in this report manganese sample are only slightly doped (less than 1%) and probably not induce a detectable shift.

The morphology of the products was examined with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and infrared (IR) spectroscopy. Figure 2 shows electron microscopy images demonstrating the morphological control of doped and undoped ZnO nanoparticles. The growth of zinc oxide exclusively in benzyl alcohol results in a heterogeneous sample where nanoparticles coexist with small rods (not shown). Cobalt doping in pure benzyl alcohol leads to rods of inhomogeneous diameter and aspect ratio (not shown), while manganese doping leads to triangular or hexagonal particles in coexistence with small rods (Fig. 2A). The use of an inert solvent (anisole) allows to control the amount of benzyl alcohol and influences the growth and hence, the morphology of the obtained zinc oxide. Figure 2B shows rods of approximately 400 × 100 nm obtained with 5% benzyl alcohol in anisole. In the case of Co-doped samples, SEM observations (Fig. 2C) demonstrate that very short rods are formed. Manganese doping leads to the formation of rods with higher average length (not shown) in the case of the synthesis with 5% benzyl alcohol in anisole. Further decrease of the benzyl alcohol content improves the aspect ratio; however, a drastic decrease of the synthesis yield is observed. Thus, in the manuscript we focused on samples synthesized with at least 5% of benzyl alcohol in

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<th>Morphology</th>
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[a] For each doped sample a paramagnetic component is always present.
anisole. Nevertheless, in order to further increase the aspect ratio, the synthesis of Co-doped ZnO was performed in pure anisole using a Teflon cup which was previously used for a synthesis of ZnO in pure benzyl alcohol (cf. also Experimental Sec.). In this case, traces of benzyl alcohol (<200 \( \mu \)L as detected by GC-MS), which were absorbed by the Teflon at high temperature, were slowly released allowing a fine control of the reaction kinetics (Fig. 2D).

Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) were used to investigate the growth orientation of ZnO. Figure 3A shows a TEM image of one rod of a cobalt doped sample. The corresponding diffraction pattern can be indexed to the hexagonal wurtzite phase of zinc oxide in agreement with XRD spectra. Furthermore, the rods are single-crystalline and elongated in the [001] direction, i.e., along the \( c \) axis. This is in agreement with the reported preferential orientation growth in solution based on the different polarity of the crystal planes.\(^{[39,40]}\) The presence of kinematically forbidden (001) reflections is often observed for ZnO nanoparticles and is caused by multiple diffraction\(^{[40]}\) and defaults. A HRTEM image recorded from the tip region of a single particle. Separations between the lattice fringes were abstracted from the power spectrum (inset) and are in agreement with the 0002 (2.60 Å) and 11–10 (1.38 Å) directions, respectively (3.88 % Co).
IR spectroscopy was performed to confirm the evolution of the morphology on the macroscopic scale. Zinc oxide presents a wurtzite structure with two transverse optical modes at $\omega_{T1} = 377 \text{ cm}^{-1}$ and $\omega_{T1} = 406 \text{ cm}^{-1}$ for bulk crystals. The bands are displaced according to the shape factor $g$. For spherical ZnO nanocrystals ($g = 0.33$), the movement of the bands is such that they overlap to give rise to a single band at 460 cm$^{-1}$. An increase in the splitting of the absorption bands takes place in going from the sphere to the cylinder. Therefore, this feature can be used to define an average fibrous grade of the ZnO particles.

Pure ZnO and Co doped ZnO made in a mixture of benzyl alcohol/anisole 5/95 % show only a broad band centered at 460 cm$^{-1}$ with and without a small splitting, respectively (Fig. 4). This is in good agreement with the TEM/SEM findings showing short rods. For the Mn doped ZnO synthesized with the same benzyl alcohol/anisole ratio the particles present a higher aspect ratio, thus the splitting is better visible and the width of the IR absorption are much sharper. The shape factor could be determined for the two latter samples, the splitting values $\Delta \nu = 120$ and 147 cm$^{-1}$, respectively correspond to $g \leq 0.02$ in good agreement with electron microscopy data.

After the morphologic characterization the concentration and homogeneity of the dopant were investigated. The doping concentration measured by ICP-AES comes out to be slightly lower than the quantity of precursors introduced (about 30 %). The cobalt concentration varies from less than 0.5 % to (larger than) 4 % depending on the amount of cobalt precursor introduced, the manganese one from 0.5 to 1 % (Table 1). In order to check the homogeneity of the cobalt distribution within the ZnO matrix, EDX spectra were recorded in the TEM (see Fig. 5). The spectra reveal that the Co concentration is homogeneous. At least, the variation of the Co concentration for different particles as well as the variations observed when measuring at different points along single particles lies below the detection limit. In addition to EDX, EELS spectra were also recorded. Due to the relatively large thickness of the particles, the Co white lines peaked only slightly above the huge background caused by the inelastic scattering processes. Again, the expected variations were below the detection limit. Therefore it can be concluded that the Co is indeed homogeneously distributed in the synthesized particles. This is also in agreement with the HRTEM investigations reported above, where no inclusions of a second phase have been observed.

In order to understand the crystal growth and the kinetic formation of ZnO, the mechanism of the reaction was studied. Nuclear magnetic resonance (NMR) was used to analyze the composition of the solvent mixture after reaction. It contains benzyl acetate as main by-product (cf. Experimental Sec.). Formation of an ester was already observed by Du et al. during the reaction of zinc acetate and ethanol and in more complex media, between zinc acetate and 1,12-dodecanediol by Joo...
et al.\cite{30} Such a synthetic approach is well established in field of nonaqueous sol-gel processes and called ester elimination.\cite{25}

The formation of zinc oxide following this route engages hydroxylation and condensation reactions (Scheme 1). During hydroxylation (Scheme 1A) the acetate functions are replaced by hydroxide groups leading to zinc hydroxide derivative and benzyl acetate. Two competitive condensation reactions can then take place: i) between two freshly formed hydroxide groups (Scheme 1B1) with the formation of water, or ii) between a hydroxide and an acetate function with release of acetic acid (Scheme 1B2). Acetic acid was not detected in final mixture probably because of its immediate reaction with benzyl alcohol producing benzyl acetate as illustrated in Scheme 1B2a. Esterification is an equilibrated reaction. However, as it took place in a large excess of alcohol the equilibrium is strongly shifted to the ester formation, thus explaining the absence of acid.

NMR quantification points to the complete reaction of acetic species with benzyl alcohol producing two benzyl acetate molecules per Zn atom. It is know that carboxylates act as surfactants in controlling the growth of nanoparticles because they bind to oxide surfaces. In a previous benzyl alcohol route it was even found that carboxylate species bind so strongly to sub-nanometer thick rare-earth oxide platelets, than they block any further growth.\cite{42} In the present case acetates cannot act as surfactants because they are totally consumed during the esterification reaction. Furthermore, water produced during the reaction could hydrolyze zinc precursors increasing overall reaction kinetics. These effects might explain the poor control over the crystal growth compared to other reactions involving benzyl alcohol.\cite{23,24}

As opposed to what was pointed out in other studies,\cite{33,41,43} the size and shape controls are not affected by the concentration of zinc precursor. Instead, the concentration of benzyl alcohol seems to play a role. This is obviously related to the fact that the concentration of zinc precursor is much smaller compared to the one of benzyl alcohol. Hence, the variation of zinc concentration does not change the kinetics of the reaction. On the other hand, reduction of the quantity of alcohol by using an inert co-solvent affects the kinetic (and probably the hydroxylation rate) as the observed aspect ratio increase substantially. Additionally, the nature and the concentration of dopants influence slightly the morphology. In the case of manganese doped particles a better morphological control can be explained by the presence of oleate molecules which behave as a surfactant.

After determining the morphology, purity, and dopant concentration, we ascertained the local environment of the cobalt using electronic spectroscopy. Diffuse reflectance UV-visible measurements of pure ZnO and ZnO doped with Co and Mn are shown in Figure 6. The spectrum of pure ZnO exhibits typical exciton bandgap absorption around 3.3 eV. Co-doped ZnO spectra show additional optical absorptions at 2.18, 2.03, and 1.9 eV due to the $^{2}A_{2}(F) \rightarrow ^{2}A_{1}(G)$, $^{4}A_{2}(F) \rightarrow ^{4}T_{1}(P)$, $^{4}A_{2}(F) \rightarrow ^{2}E_{2}(G)$ transitions which are characteristic of Co$^{2+}$ in a tetrahedral crystal field.\cite{44,45} A modification of the excitonic peak emerges after doping, which is usually attributed as a red shift of the bandgap due to sp-d exchange interactions.\cite{46–48} However, we assume that this modification is probably caused by a charge transfer as explained by Gamelin et al. in Table 1 of ref. [15]. Indeed, the bandgap edge of ZnO is still present at 3.3 eV and is only partially overlapping with this new band at around 3 eV. The spectrum of the Mn-doped sample depicts a broad absorption peak centered at 2.7 eV. Such a band is often attributed to the Mn$^{2+}$ transition $^{6}A_{1} \rightarrow ^{4}T_{1}(G)$.\cite{49,50} However, the exact origin of this band is not unequivocally assigned; by considering the width of this absorption it is justifiable to attribute it to a charge-transfer.\cite{16,51} Finally,
electron spectroscopy is in agreement with Co and Mn doped ZnO presenting a homogeneous distribution of the dopants in a tetrahedral environment.

2.2. Magnetic Properties

We complemented the study of the dopant distribution and environment with electron paramagnetic resonance spectroscopy (EPR). This technique is a very efficient tool to determine the environment of paramagnetic species in a host lattice, such as Mn in several II-VI semiconductors\cite{52-54} or Co in SnO\textsubscript{2}\cite{55}. EPR is a powerful tool for the investigation of the local structure and the distribution of the Mn\textsuperscript{2+} and Co\textsuperscript{2+} in host lattices.

EPR measurements were performed on powders. Below 1.0\% Mn doping, the spectrum shows two contributions (Fig. 7): (i) A broad resonance resulting from antiferromagnetic interactions of Mn\textsuperscript{2+} ions and (ii) a sextuplet from isolated spins (Fig. 7A). Above this Mn concentration, only a broad signal was measured at temperatures between 100 K and 300 K. The observed hyperfine splitting ($\Delta H_{pp} = 76$ Gauss, $\Delta H_{pp} = 73$ cm\textsuperscript{-1}) (Fig. 7B) is in close agreement with the bulk value for dilute Mn in ZnO matrix ($\Delta H_{pp} = 76$ Gauss) and precludes the occurrence of surface state Mn\textsuperscript{2+} atoms ($\Delta H_{pp} \sim 90$ Gauss). Contrary to a previous study on Mn doped ZnO clusters, the EPR data therefore gives no evidence for the presence of isolated surface state Mn\textsuperscript{2+} atoms coexisting with core Mn\textsuperscript{2+}\cite{56}. In the present case the manganese ions are distributed substitutionally in tetrahedral sites.

In the case of cobalt for particles synthesized in pure benzyl alcohol and in anisole with traces of benzyl alcohol a series of EPR spectra was recorded as a function of temperature (Fig. 8). At room temperature, the samples do not display any resonance. At low temperature (below 100 K), the spectra are dominated by an intense broad resonance ($H = 1500$ Gauss, $g = 4.43$) and a weaker band ($H = 3000$ Gauss, $g = 2.23$).

A deep analysis of the EPR data relies on the assignment of each resonance to the cobalt local environment. Even though the occurrence of isolated small clusters cannot grant for the observed ferromagnetic ordering at room temperature, the need to rule out cobalt clustering stands as the main focus of this study. In particular, the cobalt oxidation state needs to be enlightened by the study of Co(0) clusters to preclude any met-
al clustering in the ZnO matrix. There are few examples in the literature on the use of EPR to fully characterize cobalt based molecular clusters. The study of [Co5(μ2-S)3(P(Et3)3)]2– and [Co5MoN(CO)14AuPPh3]– show similar results. Furthermore, the samples studied in the present work do not exhibit any resonance at room temperature (Fig. 9B). Therefore, the EPR data rule out the presence of molecular clusters.

In a previous study, cobalt nanoparticles have been elaborated using chemical routes. The material consisted in a dispersion of nanoparticles displaying a narrow size distribution in a polymer matrix. The low concentration of clusters prevented the occurrence of isolated cobalt nanoparticles displaying a narrow size distribution in a matrix is very low value compared to Co clusters. Therefore, the EPR study would preclude any clustering and/or dopant reduction, we next examined the magnetic properties with a SQUID magnetometer. In the case of manganese, for all concentrations and all synthesis conditions, the pristine samples never show any deviation from a paramagnetic behavior. The ZFC-FC measurements show no deviation from Curie law (not shown). The magnetic properties of cobalt doped samples were investigated as a function of Co concentration and synthesis solvent. Magnetization versus field loops at 2 and 300 K are depicted in Figure 10 for synthesis in different solvent ratios. At low temperature, nanoparticles synthesized in benzyl alcohol/anisole (5/95) do not exhibit magnetic hysteresis for any concentration. At \( \mu_0 H = 5.0 \) T, the magnetization does not saturate and reaches values from 2.1 to 3.6 \( \mu_B/\text{Co atom} \) depending on the environment of the metal dopant determined and preclusion of any clustering and/or dopant reduction, we next examined the magnetic properties with a SQUID magnetometer. In the case of manganese, for all concentrations and all synthesis conditions, the pristine samples never show any deviation from a paramagnetic behavior. The ZFC-FC measurements show no deviation from Curie law (not shown). The magnetic properties of cobalt doped samples were investigated as a function of Co concentration and synthesis solvent. Magnetization versus field loops at 2 and 300 K are depicted in Figure 10 for synthesis in different solvent ratios. At low temperature, nanoparticles synthesized in benzyl alcohol/anisole (5/95) do not exhibit magnetic hysteresis for any concentration. At \( \mu_0 H = 5.0 \) T, the magnetization does not saturate and reaches values from 2.1 to 3.6 \( \mu_B/\text{Co atom} \) depending on the environment of the metal dopant determined and preclusion of any clustering and/or dopant reduction, we next examined the magnetic properties with a SQUID magnetometer. In the case of manganese, for all concentrations and all synthesis conditions, the pristine samples never show any deviation from a paramagnetic behavior. The ZFC-FC measurements show no deviation from Curie law (not shown). The magnetic properties of cobalt doped samples were investigated as a function of Co concentration and synthesis solvent. Magnetization versus field loops at 2 and 300 K are depicted in Figure 10 for synthesis in different solvent ratios. At low temperature, nanoparticles synthesized in benzyl alcohol/anisole (5/95) do not exhibit magnetic hysteresis for any concentration. At \( \mu_0 H = 5.0 \) T, the magnetization does not saturate and reaches values from 2.1 to 3.6 \( \mu_B/\text{Co atom} \) depending on the environment of the metal dopant determined and preclusion of any clustering and/or dopant reduction, we next examined the magnetic properties with a SQUID magnetometer. In the case of manganese, for all concentrations and all synthesis conditions, the pristine samples never show any deviation from a paramagnetic behavior. The ZFC-FC measurements show no deviation from Curie law (not shown).
on the cobalt concentration. The maximum is found for 1.16% doping (Fig. 10A). The Langevin fit gives an estimated value of $M_S = 3.6 \mu_B/Co$, close to the expected value for isolated Co$^{2+}$ (3.5 $\mu_B/Co$). The lower magnetization observed in some samples is due to an antiferromagnetic coupling between a small fraction of Co$^{2+}$ ions. At room temperature, all samples synthesized in anisole are paramagnetic (Fig. 11B). However, the samples synthesized in pure benzyl alcohol exhibit a square loop with a coercive field of 17 mT (Figs. 10B and 11). At room temperature, the magnetic moment per cobalt atom is still reaching the value of 0.80 $\mu_B$ for an applied field of $\mu_0 H = 1.0$ T (Fig. 11B). This unusual feature for a DMS makes the study of this material very interesting for application as a multifunctional (magnetic and optical) probe.

A controlled experiment on pure ZnO was performed to rule out any ferromagnetism originated from point defects (Fig. 12A). The expected diamagnetism is compensated at low temperature by a paramagnetism that certainly results from paramagnetic species absorbed on surface or intrinsic defects. However, the paramagnetism observed in this case is at least three orders of magnitude lower than in cobalt doped samples (see below).

We have also measured magnetization versus temperature ($M$–$T$ curves) (Fig. 12B). The ZFC-FC measurements show no deviation from Curie law for nanoparticles synthesized in benzyl alcohol/anisole (5/95). However, in the case of the synthesis in pure benzyl alcohol, the ZFC-FC deviate from a Curie law beyond 30 K. Above this temperature the magnetic moment is stable at a non zero value. The temperature dependence displays a behavior typical of the coexistence of ferromagnetic and paramagnetic phases. For temperatures around 35–40 K the magnetization begins to deviate from paramagnetism, as determined from a plot of the inverse magnetic susceptibility versus temperature (not shown). Therefore, the observed ferromagnetism arises from the ferromagnetically coupled Co$^{2+}$. The magnetic behavior of these nanoparticles can thus be most reasonably ascribed to a paramagnetic phase (isolated Co$^{2+}$) and a ferromagnetic phase (coupled Co$^{2+}$) in coexistence. The exchange mechanism remains unclear although the reaction conditions play a key role on the magnetic properties and in particular on the exchange interaction.

High temperature magnetization studies show that the room temperature ferromagnetism is persistent up to 900 K; the decreasing of the magnetization with temperature is sensitive to the cobalt content (Fig. 12C). The behavior of magnetization shows a non-Brillouin type temperature dependence, for various cobalt concentrations which could arise from an intrinsic magnetic effect or from thermal changes in the state of the sample with annealing temperature. It is rather intriguing and promising that the Curie temperature can be so high in an intrinsic DMS system.

For the same cobalt concentration the synthesis in pure benzyl alcohol route leads to a ferromagnetic material unlike the one in benzyl alcohol/anisole (5/95). On the other hand, the paramagnetic contribution for each sample is quantitatively related to the cobalt content and not to the solvent (Fig. 12B, inset). The nature of the solvent is only relevant to the sign of the exchange interaction between the spins, antiferromagnetic coupling for anisole, ferromagnetic coupling for benzyl alcohol. The same reaction conducted in trioctylamine also leads to a ferromagnetic material for any cobalt concentration.

Hence, the solvent plays an important role in the magnetic state and two hypotheses may arise from this statement. (i) The solvent may act as a reducing
The interactions between the Co2+ centers. (ii) On the shell 3d^7 4s^1 does not present any paramagnetic resonance due to Co(0) as already discussed from EPR measurements. Co(0) (valence 3) is likely to be present to its spin parity. In this case the formation of Co^+ might mediate the interactions between the Co^2+ centers. (ii) On the other hand, benzyl alcohol could also act as a strong σ-donor ligand on the surface. The carrier concentration would then increase from the particles synthesized in anisole to the ones in pure benzyl alcohol. Some results on nanostructured thin films have shown the effect of varying the carrier concentration by chemisorption of various reagents including amines.[64] The chemical manipulation of magnetic state in ZnO has been claimed to depend only on the carrier concentration. These results would then be in agreement with the Zener model.[2] Based on the conclusion of studies presented above, we conducted several thermal treatments in presence of the solvents used in the synthesis. The samples synthesized by the benzyl alcohol route were refluxed in anisole for 48 h in an autoclave. Their magnetic properties at room temperature are displayed in Figure 13A. The samples still exhibit a ferromagnetic behavior with no noticeable change. On the other hand, once a sample synthesized following the benzyl alcohol/anisole route has been annealed in benzyl alcohol at 250 °C for 48 h; the collected material still displays a paramagnetic behavior as shown on Figure 13B. Based on these results, we assume that the magnetic properties observed in our material are not sensitive to the surface state. The observance of ferromagnetism appears to be clearly related to the core properties of cobalt doped ZnO nanocrystals.

3. Conclusion

We have synthesized cobalt and manganese doped zinc oxide nanoparticles using a new solvent directed synthesis. The dopant substitutes onto zinc sites in the wurtzite lattice uniformly, with no detectable phase impurities or clustering. Mn-doped nanoparticles display paramagnetism for all temperature range. On the other hand, Co-doped nanoparticles exhibit a dependence of the magnetic behavior in function of the solvent used. When they are synthesized in pure benzyl alcohol they show a hysteresis effect through a wide temperature range, and display mainly ferromagnetic behavior. The magnetic moment at room temperature reaches the extremely high value of 0.8 μB/Co for very low field. The complete EPR and magnetic studies on Co doped ZnO allow to ensure that the ferromagnetic behavior is due to Co^{2+} ions. Finally, the present work brings new insights on the nature of ferromagnetism in Co doped ZnO along with the ability of elaborating very large scale amount of DMS materials without any inorganic or organic impurity.

4. Experimental

Zinc(II) acetate 99.99 %, Cobalt(II) acetate anhydrous, Anisole 99 % and benzyl alcohol 99 %, were purchased from Aldrich, stored in a dessicator (or a glovebox) and used as received. Mn(II) oleate was prepared by reacting MnCl₂ chloride and sodium oleate [65]. In a typical reaction, a Teflon cup of 45 mL inner volume was filled with 2.73 mmol of zinc(II) acetate, 16 mL of anisole and 800 μl of benzyl alcohol for the “benzyl alcohol/anisole (5/95)” synthesis or with 16 mL of benzyl alcohol for the pure benzyl alcohol route. Then, the cup was slipped into a steel autoclave, sealed and heated at 250 °C for 2 days.

Figure 12. A) ZFC magnetization curve of pure ZnO synthesized in benzyl alcohol. B) ZFC-FC magnetization curves of 0.81 % Co doped ZnO synthesized in benzyl alcohol/anisole (5/95) (full line), 4.09 % Co doped ZnO synthesized in benzyl alcohol/anisole (5/95) (dotted line), 0.77 % Co doped ZnO in pure benzyl alcohol (dashed line), 3.88 % Co doped ZnO in pure benzyl alcohol (dot-dot-dashed line), (inset) the inverse of magnetic susceptibility curves of 0.77 % Co doped ZnO in pure benzyl alcohol (unfilled round) and 3.88 % Co doped ZnO in pure benzyl alcohol (filled round) (data are normalized to the magnetic moment at 300 K).
The purpose to illustrate the decisive role of the solvent and the importance of the method is unconventional and we present here these results only with a focus on the solvent.

The larger aspect ratio obtained in this case is certainly due to the conditions of reaction. As aniseol is an inert solvent, the traces of benzyl alcohol allow the reaction. The reaction mixture, in that case, green and yellow powder were obtained (dotted line) (data are normalized to the magnetic moment of pristine sample at $\mu_0 H = 5T$). In the case of the CoII- and MnII-doped ZnO, the final reaction mixture depict: Benzyl alcohol, $\delta$(ppm): 4.55 (td, 2H, CH$_2$), 5.27 (t, H, OH, $^3$J$_{HH} = 5.4$ Hz), 7.26 (m, 5H, C$_6$H$_5$). Benzyl acetate, $\delta$(ppm): 2.07 (s, 3H, CH$_3$), 4.55 (td, 2H, CH$_2$), 7.26 (m, 5H, C$_6$H$_5$). Water, $\delta$(ppm): 3.54 (s, H$_2$O). The EPR experiments were performed at X band – 9.5 GHz on a Brucker ESP300 spectrometer with microwave powers between 0.02 and 200 mW. Temperature studies from 4.2 to 300 K were carried out using an Oxford gas-flow cryostat. Magnetic properties were measured using a SuperQuantum Interference Design (SQUID) magnetometer MPMS XL7, in the range of temperature 2–350 K and of field 0–5 T. The temperature-dependent susceptibility was measured using DC procedure. The sample was cooled to 1.8 K under zero magnetic field, low magnetic field (5–50 mT) was applied and data collected from 2 K to 350 K (zero-field cooled, ZFC). Field Cooled (FC) measurements were performed from 2 K to 350 K with an applied field during the cooling. High temperature magnetic measurements were performed on a Vibrating Sample Magnetometer (VSM) from Maglab Oxford Instrument operating at $T$ = 300–1000 K under a field of $\mu_0 H = 2$ T.

Figure 13. A) Magnetization versus field of 3.88 % Co doped ZnO synthesized in pure benzyl alcohol at 300 K (full line) and after thermal treatment in aniseole at 300 K (dotted line) (data are normalized to the magnetic moment of pristine sample at $\mu_0 H = 5T$). B) ZFC-FC magnetization curves of 4.09 % Co doped ZnO synthesized in benzyl alcohol/aniseole (5/95) (full line) and after reflux in benzyl alcohol (dotted line).

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days. The resulting suspensions were centrifuged, and the precipitates were meticulously washed with ethanol and dichloromethane and then dried in air at 80 °C. The quantity of nanocrystals produced was approximately 170 mg (yield > 70%). In the case of the Co$^{II}$- and Mn$^{II}$-doped ZnO x-equivalents of transition-metal doping were added to the reaction mixture, in that case, green and yellow powder were obtained respectively. The “aniseole with trace of benzyl alcohol” route was carried out in an autoclave previously used with benzyl alcohol only as solvent. In fact, we have quantified by GC/MS that a 45 mL Teflon cup can stock and liberate up to 200 μL of solvent inside its walls. As aniseole is an inert solvent, the traces of benzyl alcohol allow the reaction. The larger aspect ratio obtained in this case is certainly due to the continuous and slow supply of the reacting solvent. We assume that this method is unconventional and we present here these results only with the purpose to illustrate the decisive role of the solvent and the importance of the kinetic on the growth of ZnO.

The X-ray powder diffraction (XRD) data were collected on an X’Pert MPD Philips diffractometer (CuKα X-radiation at 40 kV and 50 mA). Scanning electron microscopy (SEM) images were performed using a FEG-SEM Hitachi S4100 microscope operating at 25 kV. The samples were prepared by depositing a drop of a suspension of the particles in ethanol onto a glass piece which was then coated by carbon.