Lattice distortion and its role in the magnetic behavior of the Mn-doped ZnO system

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Abstract. Puzzling magnetic data on the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ system such as a small magnetization values or a large negative values of the Curie–Weiss temperature have been obtained in many experimental investigations. Here we report element-specific structural and magnetic investigations on a high-quality $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ nanocrystalline sample. Combining low-temperature x-ray absorption spectroscopy and theoretical simulations, we show that the formation of substitutional spin-antiparallel pairs induces a large local distortion involving a contraction of the Mn–Mn distance and a reduced Mn–O–Mn bond angle. The first-principles calculation considering hole-doping reveals that such a distortion can result in a localized hole around a dopant atom, generating a ferrimagnetic ordering with a magnetization of 0.45 $\mu_B$/Mn. This result may give a new insight for a better understanding of the reported magnetic data.

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1. Introduction

Since the original report of Ohno [1], because of their expected room temperature ferromagnetic behavior, over the last decade diluted magnetic semiconductors (DMSs) have become one of the most interesting materials for future application in spintronic devices [2]. Regarding these semiconductor materials, a great deal of attention has been paid in particular to understanding the origin of the magnetic interactions. Actually, the controversy about the origin of the magnetic properties is still open and different exchange interactions between magnetic dopants and the associated distribution of dopants have been taken into consideration. Some investigations demonstrated that only carriers or bound magnetic polarons (BMPs) may give rise to a long-range ordering, e.g. when transition-metal (TM) atoms are distributed homogeneously in a host matrix [3, 4]. Other studies pointed out that a short-range exchange coupling dominates the system property, such as the double-exchange or the super-exchange interaction [5–7]. However, the predicted $T_c$ is always much lower than room temperature due to the low percolation path in the dilute ferromagnetic interaction [8, 9]. More recently, to fill the gap, it was suggested that the spinodal nano-decomposition can result in nano-magnets with high $T_c$ [10–14].

TM-doped ZnO is a peculiar type of DMS material and Mn-doped ZnO, an ideal DMS candidate, has been intensively investigated because among 3d TM atoms Mn has the largest magnetic moment. Its magnetic properties remain controversial both theoretically and experimentally. From density functional theory (DFT) calculations of the ground state of this system, both ferromagnetism (FM) and antiferromagnetism (AFM) orderings have been suggested [15, 16]. As a consequence, the calculated magnetic properties are strongly dependent on the initial structural model and the associated exchange-correlated function, including the local density approximation (LDA), generalized gradient approximation (GGA) and self-interaction corrected LDA (SIC-LDA) [17]. Parallel to the experimental magnetic data of this system, we found that its magnetic behaviors are strongly associated with the synthesis route and are also poorly reproducible. Several magnetic experiments performed on a uniform sample showed a paramagnetic configuration down to the helium temperature with a very large negative value of the Curie–Weiss temperature, which implies a strong antiferromagnetic (AFM) interaction [18–20]. In contrast, room-temperature ferromagnetism (RTF) was observed in thin films [15] and also in nano-structured samples [21–23]. Due to the fact that such samples usually contain abundant defects the appearance of RTF was usually explained by the mechanism of hole-doping [24, 25], such as Zn vacancy. Nevertheless, most of the reported experimental magnetization values are well below 0.5 $\mu_B$/Mn, much smaller than the expected value of 5 $\mu_B$/Mn for a free Mn$^{2+}$ ion [26, 27]. Therefore a better understanding...
has to be gained to integrate all the above findings. Due to the close relationship in this system between magnetic properties and structure, a careful structural investigation at the atomic level is mandatory to identify the doping positions and the distribution of TM atoms in the ZnO host matrix. In particular, as revealed in previous studies, local distortion may play an important role in the magnetic behavior of DMSs. For instance, it could enhance the AFM or FM stable ground state \[28, 29\] in different systems and reinforce the magnetization value \[30\]. As a consequence, an increasing number of investigations have been performed to reconstruct a detailed picture of these systems \[31–33\]. However, due to the very similar geometrical structure and electronic density, not much information is accessible by standard x-ray diffraction (XRD) or a transmission electron microscope (TEM). Element-selective local probes and accurate analysis are then required. X-ray absorption near-edge structure (XANES) is an element-selective tool probing the local atomic structure, successfully applied in the investigation of dopants and defect position \[25\]. In particular, with the recent development of calculations based on multiple-scattering (MS) theory, local distortion around absorber atoms can be detected through spectral simulation \[34\].

Here we present a systematic study of single-phase \(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}\) nanocrystals by means of a superconducting quantum interference device (SQUID) and low-temperature XANES combined with MS theoretical simulations and spin-polarized DFT calculations. DFT supercell calculations have been performed on candidate models to obtain relaxed lattice structures. Theoretical XANES spectra have been obtained based on MS calculations and through the comparison with experimental spectra, and thus the most suitable structural model can be selected for the following analysis. From our analysis, we may claim that Mn atoms prefer forming antiparallel substitutional pairs, in a Mn–O–Mn configuration accompanied by a large structural distortion, e.g. with a contraction of the Mn–Mn distance and a reduced bond angle of Mn–O–Mn. On the basis of this structural model, the first-principles calculation considering hole doping shows that a doping hole would be highly localized around one dopant atom, forming a ferrimagnetism (FIM) ordering.

2. Experimental and computational details

Synthesis of \(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}\) nanocrystalline samples was performed according to the method reported by Yuhas et al \[35\]. We used stoichiometric zinc acetylacetonates (2.66 mmol) and manganese acetylacetonates (0.13 mmol) dissolved in a three-neck round-bottom flask with 10.5 ml oleyamine (80–90%, ACROS) and 10.5 ml 1-octadecene (90%, ACROS) (1:1, v/v). The flask was fitted in a condenser and heated to 373 K to remove water and oxygen, with a vigorous magnetic stirring under vacuum for 20 min in a temperature-controlled electromantle. Then, under Ar atmosphere, the solution was heated to 583 K at a rate of 20 K min\(^{-1}\) and then left for 60 min at high temperature. After that, the solution was cooled to room temperature and nanocrystals were precipitated with the addition of excess ethanol. The products were washed with excess ethanol several times and dried in air at 60 °C for 3 h. The as-prepared nanocrystals were easily dispersed in a non-polar organic solvent (e.g. cyclohexane or hexane) and the color of the products is light yellow.

The sample morphology was characterized by a TEM (200CX, Jeol) operated at 160 kV and by a high-resolution TEM (HRTEM; H-9000, Hitachi) operated at 300 kV, respectively. The TEM image shows a monodispersed ZnO:Mn nanosphere with no secondary phase, while clear-cut lattice fringes appear in the HRTEM image (inset of figure 1), confirming
Figure 1. (a) TEM image of the Zn$_{0.95}$Mn$_{0.05}$O sample. Inset: an HRTEM image of the sample. (b) The temperature-dependent magnetization and the inverse of the magnetic susceptibility of the Zn$_{0.95}$Mn$_{0.05}$O sample with a magnetic field of 50 Oe. Solid lines are theoretical fits using the Curie–Weiss law. The inset shows the field dependence of the effective susceptibility measured at 3 K.

the high crystallinity of both ZnO and Mn nanocrystals. The inductively coupled plasma-atomic emission spectrum (ICP-AES; Profile Spec, Leeman Labs, USA) was measured to determine the body elemental composition, while x-ray photoemission spectroscopy (XPS) was used to characterize the surface. All data support the uniformity of the sample. Magnetization measurement was carried out with a SQUID (Quantum Design, USA) in the temperature range 2–300 K. Mn K-edge x-ray absorption spectra of Zn$_{0.95}$Mn$_{0.05}$O powder was collected at the beamline 14W of the Shanghai Synchrotron Radiation Facility (SSRF) at a temperature of 3 K. The measurement was carried out with a Si (111) double-crystal monochromator in the fluorescence mode. The electron beam energy of the storage ring was 3.5 GeV and the maximum stored current was about 210 mA. In the energy range selected for the experiments a detuning of 50% between silicon crystals was performed to suppress the high harmonic content.

All DFT calculations were performed using the CASTEP package [36], for structural relaxation. A new exchange-correlated function PBEsol was adopted to obtain accurate lattice parameters [37]. The ultrasoft pseudopotentials were constructed using the on-the-fly pseudopotential generator implemented in the CASTEP code. Plane waves are included up to the cut-off energy of 380 eV. Several doped models and the pure ZnO were modeled in $3 \times 3 \times 2$ supercells consisting of 72 atoms, using the lattice constant of the wurtzite ZnO host ($a = 3.242 \, \text{Å}, b = 3.242 \, \text{Å} \text{ and } c = 5.206 \, \text{Å}$). For the first Brillouin zone, $4 \times 4 \times 4k$-point grids were used. The XANES calculations were performed in the framework of the MS theory using the FEFF 8.4 code [38] and the structural model used the relaxation structure of the DFT calculation. The cluster potential was approximated by a set of spherically averaged muffin-tin (MT) potentials selecting the Hedin–Lundqvist model [39, 40]. A model cluster containing 126 atoms was used in all MS calculations to obtain an accurate self-consistent field (SCF) calculation, while a larger cluster (177 atoms) was used for full multiple scattering (FMS) calculations. The extended x-ray absorption fine structure (EXAFS) data were treated by IFEFFIT program [41].
3. Results and discussion

The temperature-dependent magnetization of the sample was collected under an applied magnetic field of 50 Oe and shown in figure 1(b). In the same figure is also plotted the inverse of the magnetic susceptibility (1/\(\chi\)). In the inset, the \(M(H)\) loop obtained at both 300 and 3 K is shown. Both curves do not show a magnetic hysteresis. Actually, after the subtraction of the diamagnetic background, a clear paramagnetic signal is observed at 3 K. The linear regime of the 1/\(\chi\) curve versus \(T\) in the high-temperature region, i.e. in the temperature range 150–300 K, has been fitted with the typical Curie–Weiss law behavior:

\[
[X(x)]^{-1} = \frac{T - \theta(x)}{C(x)},
\]

where \(\theta(x)\) and \(C(x)\) are the Curie–Weiss temperature and the Curie constant. Using equation (1) and setting the boundary condition \(1/\chi = 0, T = \theta(x)\) for a sample with \(x = 0.05\), we estimated a Curie–Weiss temperature \(\theta = -230\) K that points out the presence of a strong AFM interaction.

Before discussing the origin of the AFM coupling, we first have to rule out additional secondary phase contributions and confirm the position of doping ions. In figure 2(a), we show the Mn K-edge XANES spectrum of the \(\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}\) sample after the background subtraction and normalization in the region 6530–6605 eV. For comparison, from top to bottom we also show in the same panel experimental spectra at the Mn K-edge of Mn metal, MnO, \(\text{Mn}_3\text{O}_4\) and MnO\(_2\). All spectra are in good agreement with previous investigations [42, 43]. Major differences occur in the overall oscillations between the sample spectrum and spectra of standards, pointing out the lack of such phases in our sample. As shown by Titov et al [44],
Table 1. Parameters of the fit of the Mn-doped ZnO sample. $N$ is the coordination number. $R$ is the distance between the Mn central atoms and surrounding coordination atoms. $\Delta E$ is the difference between the zero kinetic energy value of the sample and that of the theoretical model. $\sigma^2$ is the mean square disorder.

| Sample     | Pair | $N$  | $R$ (Å) | $\Delta E$ (eV) | $\sigma^2 \times 10^{-3}$ (Å$^2$) |
|------------|------|------|---------|----------------|---------------------------------|
| Zn$_{0.95}$Mn$_{0.05}$O | Mn–O | 3.6 ± 0.5 | 2.04 ± 0.02 | −1 | 4 ± 1 |
|            | Mn–Zn | 11.4 ± 1.0 | 3.24 ± 0.02 | −5 | 10 ± 2 |

the analysis of the pre-edge features originating from the p-d hybridization offer important electronic information, probing the Mn charge state in tetrahedrally coordinated magnesium oxide compounds. A single pre-peak indicates the presence of the $d^5$(Mn$^{2+}$) configuration, while a double pre-peak refers to the $d^4$(Mn$^{3+}$) configuration. In our spectra the occurrence of a single peak at the Mn edge supports the occurrence of a Mn$^{2+}$, a condition that agrees with a substitutional inclusion of Mn ions in the ZnO ordered matrix. Quantitative information can be obtained by the EXAFS analysis using IFEFFIT as listed in table 1. In the fitting process, due to the consideration of phase correction, the results of the bond lengths are more accurate than the megascopic value from the Fourier transforms. Data indicate that Mn fits in a tetrahedral structure with a Mn–O bond length of 2.04 Å, very close to the value of the Mn$^{2+}$ ion in Mn$_3$O$_4$ (2.035 Å), but shorter than the typical bond length of a sixfold coordinated environment such as MnO (2.26 Å). Typical MnO bond lengths in other materials are $\sim$ 2.02 Å (Mn$_2$O$_3$) and 1.88 Å (MnO$_2$). From the experimental point of view, due to the fact that the XANES is a technique reflecting the mean effect at different atomic positions, it is hard to distinguish Zn–O bond lengths near dopants and far away from these sites. Thus, the Zn–O bond length (1.98 Å) is the average value characterized by both XRD and HRTEM, obviously shorter than the Mn–O bond length (2.04 Å). It then points out the occurrence of a lattice distortion induced by the Mn doping. Moreover, the Mn–Zn(Mn) distance of 3.24 Å is consistent with the value of the ZnO wurtzite structure [45]. We need to stress here that these bond values are average values that do not really reproduce all details of the Mn structure. However, combining XANES data and the results of the EXAFS fit, we may rule out in our sample the presence of additional secondary phases and confirm the occupation of Zn sites by Mn atoms. As a consequence, data fully support the hypothesis that the AFM coupling is an intrinsic property of the sample rather than a property arising from a phase separation.

In addition, other details can be obtained by XANES simulations to recognize features due to MS contributions, sensitive to the local three-dimensional (3D) arrangement. We performed also a DFT supercell calculation to obtain the relaxed structure and use these models as the input for XANES simulations. Before, in order to guarantee the reliability of calculations by using different exchange functions, both GGA-PBE and PBEsol exchange functions can be used for DFT calculations on a wurtzite-type Zn$_{36}$O$_{36}$ supercell. The results show that theoretical lattice parameters obtained by PBEsol are very close to experimental data, whereas GGA-PBE overestimates them by $\sim$1.5–2%. To simulate the Mn distribution of different concentrations and the different relative positions, we used a periodic $3 \times 3 \times 2$ wurtzite supercell of ZnO containing 72 atoms in a unit cell and in which we introduced six different sites as described in figure 3(h). The presence of different sites is based on the consideration that the Zn–O
Figure 3. Comparison of the Mn clusters in the ZnO host for different cluster sizes and distribution of electronic/spin states. We introduced in the ZnO $3 \times 3 \times 2$ supercells six different sites labeled from 1 to 6 (see (h)) occupied by Mn atoms, selectively. Mn, Zn and O atoms are displayed as magenta, gray and red spheres, respectively. In panel (i), as an indicator of the magnetic stability of the different models we plot the energy difference between the FM and the AFM ordering ($\Delta E = E_{AFM} - E_{FM}$). The dotted line corresponds to $\Delta E = 0$ and indicates when equivalent FM and AFM orderings occur.
Figure 4. (a) Comparison of Mn K-edge XANES spectra of different models of the Mn-doped ZnO system with the experimental spectrum of the Zn$_{0.95}$Mn$_{0.05}$O sample (bottom). The top spectrum corresponds to the ideal Mn$_{Zn}$ substitutional model, while the four spectra in the middle correspond to optimized models. (b) Comparison of Mn K-edge experimental XANES spectra of the Zn$_{0.95}$Mn$_{0.05}$O sample with calculated spectra in the dimer model with different magnetic orderings, corresponding to the (c) magnified local structure including the bond lengths and bond angles for two magnetic orderings.

ground state has an AFM ordering, with an FM state at about 77 meV per Mn atom higher in energy. To reduce the number of candidate cluster configurations, we pick that with the lowest energy among the supercells containing the same number of Mn atoms, i.e. configurations (a), (c), (d) and (g). The choice of the model is similar to that of the previous report in the Co-doped ZnO system [46] and the clustering behavior of magnetic atoms is a general feature of TM-doped semiconductors.

Theoretical Mn K-edge XANES spectra have been calculated using the chosen configuration by the FEFF 8.4 code. Simulated spectra are compared with experimental data in figure 4(a). All spectra exhibit similar oscillations, pointing out that Mn doping does not modify the host lattice. Still, the intensity of the feature $E$ in all relaxed structures decreases relative to the spectrum without optimization. In particular for the Mn-pair model the peak intensity significantly decreases, in good agreement with the experimental behavior. Actually, this feature is strongly correlated with the local structure and to changes induced by external conditions or different chemical environments already observed in previous investigations. For instance, investigations performed in high-pressure conditions by Pellice-Porres et al [45] pointed out a strong increase in the intensity of the peak $E$ at pressure > 9.3 GPa. In particular, the intensity of this feature significantly decreases when numerous Zn vacancies ($V_{Zn}$) appear in the Zn$_{0.97}$Mn$_{0.03}$O sample [25]. In our samples, by careful analysis of ICP-AES data, we may rule out the contribution of $V_{Zn}$ with no evidence of a large unstoichiometry. Moreover,
Figure 5. (a) Schematic energy levels of two interacting Mn atoms with the spins aligned parallel or antiparallel with the highest occupied level fully or partially filled. (b) The DOS of the ZnO system doped with two Mn atoms. The upper and lower panels correspond to the hole-free and one hole-doping magnetic stable ground state.

from MS calculations, using different clusters of variable sizes around the photoexcited atom, similar to Wu et al [47], we recognized that this feature originates from backscattering events occurring in the second cation shell, in agreement with previous work [48]. Thus, by means of DFT calculations combined with MS analysis, we confirm that in these samples large lattice distortions occur and Mn dopants prefer spin-antiparallel pair configurations in the ZnO matrix.

In the following, we will discuss the influence of spin-antiparallel Mn pairs on the ZnO host structure and, for comparison, we show in figure 4(c) the calculated structure of FM ordering and the corresponding calculated spectra (figure 4(b)). In the latter case, we did not observe significant changes and also the structural symmetry is well retained, i.e. the Mn–O bond lengths are 2.03 and 2.05 Å for in-plane and out-plane, respectively, while the Mn–Mn distance is 3.25 Å, close to that in ZnO. Finally, the Mn–O–Mn bond angle decreases from 110.8° to 106.2°. In contrast, several large changes occur in the AFM case: (i) the Mn–O bond length associated with another Mn (2.01 Å) is 0.05 Å shorter than that with Zn (2.06 Å), pointing out a distorted tetrahedral geometry around dopants; (ii) the bond angle Mn–O–Mn significantly decreases, i.e. it decreases down to 101°; (iii) the Mn–Mn distance shortens from 3.25 to 3.11 Å, while the Mn–Zn bond length slightly increases. Structural data indicate that Mn atoms are close to each other and the second coordination shell exhibits a large distortion probably at the origin of the decrease of intensity of the feature E observed in the XANES spectrum. The strong related behavior between the structural distortion and the magnetic coupling has also been discussed in the Mn-doped GaN film, another class of DMSs, in which DFT calculations indicated a shortening of the Mn–Mn distance at the surface (2.98 Å) from that of the bulk of 3.11 Å. The decrease of the bond has also been associated with a transition from an FM to an AFM configuration [49]. Actually, it has been established that the magnetic coupling between Mn atoms is very sensitive to the Mn–Mn distance, a condition that causes the Mn-based compound to exhibit different magnetic phases ranging from AFM to low-spin FIM and high-spin FM [50, 51].

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As discussed in a previous investigation of Mn-doped/Co-doped Cu$_2$O [52] or Co-doped ZnO [53], the preferred magnetic ground state may be identified looking at the two-level models [54]. Figure 5(a) shows the schematic energy level layout for two neighboring Mn atoms with both spin arrangements (AFM and FM) and the highest occupied level fully or partially filled. A set of bonding–antibonding states for each spin channel is formed on the Mn atom due to the interaction between the up- and down-spin states via the spin-conserving hopping matrix element $t$. In the FM arrangement, both bonding and antibonding levels of one spin channel are completely filled so that no energy gain can be obtained with this coupling. In contrast, in the AFM arrangement bonding states are fully filled, while antibonding states are empty, leading to an AFM energy gain $\propto t^2/I$, where $I$ is the energy separation of the spin levels for Mn. Hence, in this case the AFM ground state is stable. In contrast, if we consider the presence of one hole introduced by defects such as a Zn vacancy occurring in a typical growth process, the reduction of the occupation of Mn d states in the majority-spin channel may occur and a significant FM ordering may also result in an energy gain and competition between AFM and FM arrangements. Thus, we performed a careful calculation as shown in figure 5(b) of the projected partial density of states (DOS). Due to the tetrahedral crystal field, Mn 3d states may be described by states with both $e$ and $t_2$ symmetry. The majority $t_2$ states and the minority $e$ states are located in the gap. After one hole is introduced in the structure, an asymmetric DOS appears and a part of it pins at the Fermi level, generating a FIM ordering with a magnetization of 0.45 $\mu$B/Mn. In this configuration, the local magnetic moment of each Mn, antiparallel, has different amplitudes. The behavior is strongly related to the strong coupling between a localized hole and the spin, which results in a Zhang–Rice (ZR)-like state, with a sign reversal of the apparent p–d exchange integral, as reported by Dietl [55]. A similar result was also shown in the Fe-doped GaN system in a previous theoretical investigation [56].

The result also indicates that in this system, even in the case of the hole-doping system, a spin-antiparallel arrangement is energetically favored. This finding gives new insight into the observation of a weak FM in other experimental reports [21–23].

4. Conclusion

Summarizing, the puzzling magnetic data regarding Mn-doped ZnO can now be interpreted with a new atomic local structural model. In this paper, we report an extensive investigation, including magnetic and element-specific structural characterizations, of a high-quality Zn$_{0.95}$Mn$_{0.05}$O nanocrystalline sample. The system exhibits paramagnetic behavior accompanied by a large negative Curie–Weiss temperature. X-ray absorption spectroscopy data collected at 3 K have been used to characterize the local structure around Mn-dopant atoms. Spectra have been simulated within the framework of the well-established MS theory and combined with spin-polarized DFT calculations. The results indicate that Mn ions fill only Zn sites, forming spin-antiparallel pairs and inducing a large structural distortion, e.g. a contraction of the Mn–Mn distance and a reduced bond angle of Mn–O–Mn. Moreover, first-principle calculations considering hole doping reveal that such a distortion can result in a localized hole around the dopant atom, forming a FIM ordering with a magnetization of 0.45 $\mu$B/Mn. On the basis of this finding, the controversial magnetic properties of this system could be understood. The Mn-doped ZnO system presents substantial paramagnetic behavior and the strong AFM interaction arises from the fact that Mn dopants prefer forming a configuration with spin-antiparallel pairs. The weak FM observed in the hole-doping samples is actually a FIM.
these results address the critical role of the lattice distortion in the magnetic behavior of the Mn-doped ZnO system and, more generally, of many other DMSs.

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