X-ray absorption study of the local order around Mn in Mn:ZnO thin films: the role of vacancies and structural distortions.

C. Guglieri^{1,2}, E. Céspedes³, C. Prieto³ and J. Chaboy^{1,2}

¹Instituto de Ciencia de Materiales de Aragón, Consejo Superior de Investigaciones Científicas - Universidad de Zaragoza, 50009 Zaragoza, Spain

²Departamento de Física de la Materia Condensada, Universidad de Zaragoza, 50009 Zaragoza, Spain.

³Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco 28049 Madrid, Spain.

Abstract.

This work reports an X-ray absorption near-edge structure spectroscopy (XANES) study at both Mn and Zn K-edge in $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ thin films prepared with different sputtering gases (pure Ar, Ar/N₂ and Ar/O₂). We have studied the local order around Mn in the films, with special emphasis in the role played by both oxygen and zinc vacancies and by the structural distortion associated with the substitution of Zn by Mn in the ZnO host. Our results indicate that the dependence of the magnetic properties of these Mn:ZnO thin films with the different sputtering gas used in the preparation is related to the structural distortion around Mn sites.

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1. INTRODUCTION

The development of oxide-based diluted magnetic semiconductors (DMS) with high Curie temperatures has attracted much attention in recent years due to its great functionalities in spintronic devices [1, 2, 3, 4]. In particular, Mn–Zn–O system has been widely studied and large efforts have been aimed at finding Curie temperatures over room temperature (RT), which results an essential fact to build magneto-opto-electronic devices. T_C higher than RT has been achieved for Mn–Zn–O films prepared by different methods [5]. However, the full understanding of the origin of the observed magnetism in transition-metal doped ZnO systems has not been obtained yet and there are debates whether this is caused by defects other than the metal dopants. To date, several types of defects, such as oxygen and zinc vacancies, as well as hydrogen, oxygen and zinc interstitials, have been proposed by different authors to induce high-temperature ferromagnetism (HTFM) in ZnO-based DMSs [6, 7, 8, 9, 10, 11].

Aiming to determine the exact type of defect that causes the HTFM in these systems several experimental tools, as X-ray absorption spectroscopy (XAS), have been applied. However, based on similar experimental spectra, different authors report opposite conclusions regarding the nature of defects involved in the observed HTFM. Hsu et al. [12] have concluded that oxygen vacancies enhance room-temperature ferromagnetism in Co-doped ZnO films while, on the contrary, Yan et al. [13] concluded that Zn vacancies induce room-temperature ferromagnetism in Mn-doped ZnO. This scenario is further complicated by the results of Zhang *et al.* [14] who concluded from similar data that the aforesaid oxygen vacancies are located in the second shell around magnetic ions. These results pose serious doubts about the real capability of X-ray absorption spectroscopy to determine the presence of vacancies in these systems and, consequently, to shed light on the origin of the magnetism in these systems.

Here, we present an X-ray absorption near-edge structure spectroscopy (XANES) study performed at both Mn and Zn K-edge in $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ thin films prepared with different sputtering gases (pure Ar, Ar/N₂ and Ar/O₂). The magnetic properties of these samples differ as a function of the different gas using during the preparation [15, 16]. Contrary to similar studies focussed in the role of vacancies, Céspedes *et al.* pointed out the relationship of this behaviour with the Mn short-range order in the lattice [15], as in similar ZnMnO systems [17, 18]. With this in mind, we have performed a detailed study of the local order around Mn in Mn:ZnO thin films by means of *ab-initio* XANES calculations. During this study, a special emphasis has been paid to determine the role played by both vacancies and structural distortions.

2. COMPUTATIONAL METHODS

The computation of the XANES spectra was carried out using the multiple-scattering code CONTINUUM [19] based on the one-electron full-multiple-scattering theory [20, 21]. A complete discussion of the procedure can be found elsewhere [22, 23].

The potential for the different atomic clusters was approximated by a set of spherically averaged muffin-tin (MT) potentials built by following the standard Mattheis' prescription. The muffin-tin radii were determined following the Norman's criterion and the overlapping factor between the muffin-tin spheres was fixed to 1%. It should be stressed that no free parameter has been used during the calculations. The theoretically calculated spectra have been directly compared to the experimental XANES spectrum i.e., no fitting procedure has been used. The assessment of the quality of the theoretical computations is based on the correct reproduction of the shape and energy position of the different spectral features and of their relative energy separation and the intensity ratio. In all the cases, the theoretical spectra have been convoluted with a Lorentzian shape function to account for the core-hole lifetime ($\Gamma=1.2$ eV) [24] and the experimental resolution ($\Gamma=1$ eV).

3. RESULTS AND DISCUSSION

The experimental spectra recorded at both the Mn and Zn K-edge in the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ films prepared with different sputtering gas are shown in Fig. 1. They are compared to the Mn K-edge spectra recorded for a $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ thin film by Pellicer-Porres *et al.* [25] and to the theoretical computations performed by Yan *et al.* [13].

The Mn K-edge spectra of the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ films prepared with different sputtering gas are similar in the high energy region to those previously reported by Pellicer-Porres *et al.* [25]. However the intensity ratio between the main absorption line and the first broad resonance (~ 15 eV above the main line) is markedly different in both cases. It should be noted to this respect that the computations reported by both Yan *et al.* [13] and Pellicer-Porres *et al.* [25] fail into reproducing this intensity ratio. Despite the poor agreement between the theoretical calculations and the experimental data in the near-edge (XANES) region, several authors conclude from their comparison the existence of both oxygen and zinc vacancies to whom the HTFM observed in the materials is addressed [12, 13, 14].

The fact that the analysis of similar experimental spectra leads to opposite conclusions poses the question about the reliability of these assignments as well as of the capability of X-ray absorption spectroscopy itself to determine the presence of vacancies in the materials under study. Indeed, the determination of the presence of vacancies from the XANES spectra is not an easy task. It should be noted that the conclusions previously reported were derived from the occurrence of subtle changes in the intensity of different spectral features through fingerprint comparisons of *ab-initio* computations and the experimental data. Consequently, a convincing demonstration of the influence of the vacancies on the XANES spectra, beyond qualitative fingerprint analysis, is still missing.

To get a deeper insight in this problem we have performed an accurate and systematic *ab-initio* computation of both the Mn and Zn K-edge XANES spectra

Figure 1. (color online) Top panel: Comparison between the experimental Mn K-edge XANES spectra of Ar, Ar/N₂ and Ar/O₂ prepared Zn_{0.95}Mn_{0.05}O films and: a) the experimental data reported in Ref. [25] for Mn in ZnO rock-salt (RS) and in ZnO wurtzite (W) structures (left), and b) calculations reported in Ref. [13] for Mn substituting Zn in stoichiometric W structure (MnZn), W with oxygen vacancies (MnZn+VO), and W with zinc vacancies (MnZn+VZn). Bottom panel: Comparison of the Zn K-edge XANES spectra of Ar, Ar/N₂ and Ar/O₂ prepared Zn_{0.95}Mn_{0.05}O films.

in $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ films. The first step of our study has been to perform the XANES calculation for reference compounds in order to determine the best choice of several computational parameters as the cluster-size, overlapping factor, exchange and correlation potential, etc. After fixing these computational parameters we have focussed in the study of the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ films. For these systems the XANES spectra have been calculated for a simple substitutional model in which Mn substitutes Zn in the wurtzite structure. This calculation has been extended by considering the presence of both O and Zn vacancies near the photoabsorbing atom, either Mn or Zn. Following the results of Kuzmin *et al.* we have not considered the off-centre displacement of the photoabsorbing ions [26].

3.1. Ab-initio XAS Calculation for Reference compounds

We have calculated the Zn K-edge XANES spectra of ZnO in both wurtzite, ZnO-*W*, and rocksalt, ZnO-*RS*, structures. The results have been compared to the experimental spectra reported by Decremps *et al.* [?]. In addition, we have calculated the Mn K-edge XANES of MnO.

The comparison of the experimental Zn K-edge XANES spectrum of ZnO-*W* and the theoretical computations is reported in Fig. 2. Computations have been performed by using a cluster containing 177 atoms, i.e. including the contributions for atoms within the first 8 Å around photoabsorbing Zn. These calculations have been performed by using four different exchange and correlation potentials: HL, Hedin-Lundqvist complex potential; DH, real Dirac-Hara ECP; *real* HL, in which only the real part of the HL ECP is used; and *complex* DH, that is built up by adding to the Dirac-Hara ECP the imaginary part of the HL one. As shown in Fig. 2, the computations account for all the spectral features: the main absorption peak (B) at ~ 7.5 eV above the absorption edge; the three-peaks structure centered at about 20 eV above the edge ($D_1 \sim 18$ eV, $D_2 \sim 21$ eV, $D_3 \sim 26$ eV); and the two broad resonances, G and I, at higher energies ($G \sim 53$ eV, $I \sim 77$ eV). Despite all the computations made with both HL and DH ECPs reproduce all the experimental spectral features, the relative energy separation among these features is poorly reproduced by using HL potentials. On the contrary, the agreement between the theoretical spectra and the experimental one is remarkable when DH ECP is used.

The fact that the HL potential leads to a contraction of the energy scale of the computation has been previously addressed in a variety of systems [28, 29, 30, 31, 32, 33]. These works shown that, as in the present case, the absorption maxima calculated by using the HL ECP fall short the experimental ones, specially regarding the energy region between 30 and 70 eV above the edge. In the particular case of ZnO, this anomalous contraction, evident from the inspection of the energy separation of the three well resolved negative dips ($C \sim 14$ eV, $E \sim 35$ eV and $H \sim 62$ eV), has been also reported by independent calculations [?, 34] although no comment was deserved. It

Figure 2. (color online) Top panel: Comparison between the experimental Zn K-edge XANES of wurtzite ZnO (•) and the computations performed by using real exchange and correlation potentials: DH (blue, solid line) and *real* HL (red, dashed). Bottom panel: Same as above in the case of *complex* ECPs: *complex* DH (blue, solid line) and HL (red, dashes). (See text for details).

should be noted that this drawback is not associated with the use of overlapping atom potentials versus SCF potentials. The SCF potentials can lead to an improvement of the Fermi level determination in such a way that typical errors in the Fermi level are $\sim 1 \text{ eV}$ and $\sim 3 \text{ eV}$ with self-consistent and overlapped atom potentials calculations, respectively. However, it has been previously demonstrated that the DH ECP improves the HL performance no matter whether the SCF or non-SCF method is used [35].

As shown in Fig. 3, similar results have been found in the computation of the Zn K-edge of Zn in rocksalt ZnO and of the Mn K-edge in MnO (see also Fig. 9 in the Supplementary Information). In both cases the size of the cluster has been chosen (200

Figure 3. (color online) Top panel: Comparison between the experimental Zn K-edge XANES of rocksalt ZnO (•) and the computations performed by using both real (red, dashes) and *complex* (blue, solid line) Dirac Hara ECPs. Bottom panel: Comparison of the experimental Mn K-edge XANES spectrum of MnO and the computations performed by using complex ECPs: complex DH (blue, solid line) and HL (red, dashes).

atoms for ZnO-*RS* and 179 atoms for MnO) to include the contribution of atoms within the first 8 Å around the photoabsorbing atom, as in the case of ZnO-*W*. In the Zn K-edge computations for both ZnO-*W* and ZnO-*RS* the use of complex potentials introduces an excessive damping of the XANES spectra. In these cases the best agreement with the experimental data is obtained by using the real DH exchange and correlation potential. By contrast, the Mn K-edge XANES spectrum of MnO is best reproduced by adding to the DH ECP the the imaginary part of the HL self-energy. It should be noted that even if a fitting procedure based on absorption signals calculated in the MT approximation provides sometimes excellent fits to the experimental spectra, this approach is not predictive. Indeed it may lead to false minima when the program tries to compensate a deficiency of the optical potential by changing the value of some other correlated parameters. Being our main aim to evaluate the modifications of the absorption spectra

induced by the presence of vacancies, presumed *a priori* quite small, we have performed the calculation of the absorption spectrum without using any adjustable parameter.

Following these prescriptions we have calculated the Mn K-edge XANES spectra of Mn:ZnO systems showing both the wurtzite and rocksalt structures. The theoretical spectra have been compared to the experimental spectra reported by Pellicer *et al.* [25]. As shown in Fig. 4, the computation performed by considering that Mn substitutes Zn in the ZnO-*RS* structure is well reproduced by the calculation. However, the agreement worsens in the case of ZnO-*W*. The fact that the XANES spectrum of the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ thin film in the rocksalt structure is well reproduced by the computation while the same does not hold for the same system in the wurtzite structure. This result suggests that the presence of vacancies is not the main responsible of the disagreement between the theoretical and the experimental spectra of the wurtzite case, especially if one takes into account that only one atom, the photoabsorber, has been changed in clusters of 200 and 177 atoms for rocksalt and wurtzite, respectively.

3.2. *Ab-initio XAS Calculation of $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ Thin Films: role of vacancies*

Aimed at verifying the role of vacancies into modifying the XANES spectral shape of the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ films prepared with different sputtering gas we have performed several theoretical calculations by imposing the presence of both oxygen and zinc vacancies in the first coordination shells of the photoabsorbing atom. These calculations have been performed at both the Zn K-edge and Mn K-edge in Mn:ZnO-*W*. In all the cases the interatomic distances have been kept fixed as in the undoped ZnO-*W*. The Mn K-edge spectra have been calculated by simply substituting Mn by Zn at the photoabsorbing site. It should be noted that it is expected that the presence of vacancies induces subtle changes to the spectra. By this reason we display hereafter the result of the computations obtained by using the real Dirac-Hara in order to get an enhanced view of these changes.

Fig. 5 reports the results of the calculation of the Zn K-edge XANES spectra performed on a 177 atoms cluster in which the oxygen atoms have been progressively removed from the first coordination shell of the photoabsorbing Zn. The presence of a single oxygen vacancy in the tetrahedron surrounding Zn affects the whole spectral shape, i.e. the relative intensity of all the spectral features is modified. In particular, the characteristic three peaks structure centered at ~ 30 eV above the edge is completely modified and the intensity ratio of the three (D_1 , D_2 and D_3) peaks is reversed. This is the expected result, contrary to previous reports [12], because the oxygen vacancy affects not only the single scattering process in the first coordination shell of Zn, but also many of the multiple scattering paths contributing to the X-ray absorption spectrum. Including further oxygen vacancies in the next-neighbouring tetrahedron enhances these differences and changes this structure, characteristic of wurtzite, completely and the theoretical spectrum does not resemble the experimental one. By contrast, the inclusion

Figure 4. (color online) Comparison between the experimental Mn K-edge XANES of Mn:ZnO (●) and computations performed by considering that Mn substitutes Zn in the wurtzite ZnO structure. Computations have been done by using both DH (top panel) and HL (bottom panel) ECP potentials.

of Zn vacancies in the second coordination shell does not modify significantly the spectral shape. Indeed, only a slight decrease of the white line intensity and of the main absorption features is found upon increasing the number of Zn vacancies appearing simultaneously in the second coordination shell.

It has been previously reported that upon removing one oxygen atom from the first coordination shell a new peak appears in the preedge region and that its intensity becomes more pronounced if a second oxygen vacancy is created in the second oxygens coordination shell [12]. Beyond the lack of agreement with our calculations, this model is not reliable as it considers an *ad hoc* arrangement of vacancies. If the oxygen vacancies are randomly distributed, the probability of photoabsorbing Zn having n vacancies in the first coordination shell can be calculated by a simple binomial distribution as $P(n) = \binom{4}{n} x^n (1-x)^{4-n}$ where x is the concentration of oxygen vacancies. Accordingly, the Zn K-edge XANES spectrum should correspond to the addition of spectra with and

Figure 5. (color online) a) Comparison of the theoretical Zn K-edge XANES spectrum of ZnO- Wurtzite (black, solid line) and those calculated by considering the existence of oxygen vacancies (V_o) in the first coordination shell of photoabsorbing Zn: $1V_o$ (red, dots), $2V_o$ (green, dash), $3V_o$ (blue, dot-dash) and $4V_o$ (cyan, short dot-dash-dot). b) a) Comparison of the theoretical Zn K-edge XANES spectrum of ZnO- Wurtzite (black, solid line) and those calculated by considering the existence of Zn vacancies (V_{Zn}) in the second coordination shell of photoabsorbing Zn: $1V_{Zn}$ (red, dots), $2V_{Zn}$ (green, dash), $3V_{Zn}$ (blue, dot-dash) and $4V_{Zn}$ (cyan, short dot-dash-dot). In all the cases computations have been performed by using the *real*-DH ECP to enhance the differences.

without oxygen vacancies around the photoabsorbing Zn atom weighted according to this probability. As shown in Fig. 6, the effects induced by the presence of oxygen vacancies are undetectable for defect concentrations of up to 50 %.

Similar results are found in the case of the Mn K-edge XANES of the $Zn_{0.95}Mn_{0.05}O$ films. As shown in Fig. 7, the presence of either O or Zn vacancies in the next neighbouring shells around Mn would affect the intensity of all the spectral features and not only of the pre-edge region. As in the case of the Zn K-edge, these effects become undetectable in the XANES spectra when the vacancies are randomly distributed. This is shown in panel c) of Fig. 7 for an oxygen defect concentration of up to 50 %.

Figure 6. (color online) Comparison of the theoretical Zn K-edge XANES spectrum of ZnO- Wurtzite (black, solid line) and those calculated by considering the existence of oxygen vacancies (V_o in the first coordination shell of photoabsorbing Zn and by assuming a binomial distribution of the oxygen vacancies with different defects concentration: no vacancies (black, solid line), 5 % (red, dots), 10 % (green, dash), 20 % (blue, dot-dash) and 30 % (cyan, short dot-dash-dot).

All these results indicate that the existence of both oxygen and Zn vacancies in the Mn:ZnO films have little influence on the absorption spectra recorded at both Zn and Mn K-edge. Indeed, the theoretical computations presented here point out that if reliable concentration of defects, randomly distributed, is taken into account, the effect of vacancies on the XANES spectra is negligible. More importantly, even maximizing their effect by choosing *ad hoc* defect distributions it is not possible to recover the Mn K-edge experimental spectrum of the Mn:ZnO film in the wurtzite structure.

3.3. Ab-initio XAS Calculation of $Zn_{0.95}Mn_{0.05}O$ Thin Films: role of structural distortions

The results presented in the previous sections suggest that the disagreement of the theoretical computations and the Mn K-edge of the $Zn_{0.95}Mn_{0.05}O$ thin film in the wurtzite structure is not due to the presence of vacancies. In this situation, structural modifications, induced by the Mn substitution at the Zn site, appear as the best explanation to account for the disagreement between the theoretical and experimental spectra.

Despite that several authors have shown that the substitution of Zn by Mn induces a structural distortion in the next neighbouring environment of the absorbing atom [16, 36], all the computations performed for these systems looking for the presence of vacancies have been done by considering that Mn substitutes Zn in both the ZnO-*W* and ZnO-*RS* structures without modifying the interatomic distances. In the case of

Figure 7. (color online) a) Comparison Mn K-edge XANES spectrum of Mn:ZnO-Wurtzite (●) and the theoretical calculations performed by considering the existence of Zn vacancies (V_{Zn}) in the first coordination shell of photoabsorbing Zn: no vacancies (black, solid line), $1V_{Zn}$ (red, dots), $6V_{Zn}$ (blue, dash), and $12V_{Zn}$ (green, dot-dash). b) Comparison Mn K-edge XANES spectrum of Mn:ZnO-Wurtzite (●) and the theoretical calculations performed by considering the existence of oxygen vacancies (V_o) in the first coordination shell of photoabsorbing Zn: no vacancies (black, solid line), $1V_o$ (red, dots), $3V_o$ (green, dash), and $4V_o$ (blue, dot-dash). c) Same as b) by considering a binomial distribution of a 50% of oxygen vacancies.

ZnO-*RS*, the nearest-neighbours interatomic distance is $R_{Zn-O} = 2.14$ Å, while $R_{Zn-O} = 1.97$ Å in ZnO-*W*. This nearest-neighbours interatomic distance is $R_{Mn-O} = 2.22$ Å in MnO. Therefore, it seems reasonable to think that when entering in the ZnO-*W* structure, Mn adapts the original ZnO_4 tetrahedron by enlarging the R_{Mn-O} distances. Accordingly, this effect should be less marked in the case of ZnO-*RS* because the R_{Zn-O} distance is closer to the R_{Mn-O} of MnO than in ZnO-*W*. In this way, it should be possible to understand why the experimental Mn K-edge XANES spectrum of the $Zn_{0.95}Mn_{0.05}O$ thin film in the rocksalt structure is well reproduced by the theoretical computations performed by assuming a simply Zn-Mn substitution while that in the wurtzite structure does not.

To verify this hypothesis we have calculated the Mn K-edge XANES spectrum of Mn:ZnO in the wurtzite phase by considering that Mn substitutes Zn in the ZnO-*W* frame and, in addition, by increasing progressively the interatomic R_{Mn-O} distance in the nearest-neighbours shell of Mn (MnO_4 tetrahedron) from 1.97 Å, ZnO-*W*-like, to 2.22 Å, as in MnO. As shown in Fig. 8, the computation performed considering a $R_{Mn-O} = 2.03$ Å yields a good reproduction of the experimental spectrum, especially regarding the broad resonance C, ~ 20 eV above the edge, and the intensity ratio between this resonance and the white-line (peak B). Moreover, the computation exhibits a shift towards lower energies of the edge position, as expected because the R_{Mn-O} increases, and the structure at the raising edge is slightly enhanced with respect to the computation in which Mn simply substitutes Zn without modifying the interatomic distances. The occurrence of an enlarged Mn-O interatomic distance is also in agreement with EXAFS results [25]. Finally, we have also checked in this case that adding an oxygen vacancy in the first coordination shell of Mn has no effect on the calculated spectrum.

This behaviour is in agreement with the modification observed in the XANES of the $Zn_{0.95}Mn_{0.05}O$ thin films prepared by using different sputtering gas (see bottom panel of Fig. 8). This points out that the variation of the reported HTFM in Ar- $Zn_{0.95}Mn_{0.05}O$ and Ar/ N_2 - $Zn_{0.95}Mn_{0.05}O$ samples, diminishing the ferromagnetic response when using Ar/ N_2 , is mainly associated with dissimilar Mn local structures in both samples. On the other hand, as shown in Fig. 8, there are some differences between the XANES spectra of these samples and that reported by Pellicer *et al.* [25]. The Mn K-edge XANES spectra of both Ar- $Zn_{0.95}Mn_{0.05}O$ and Ar/ N_2 - $Zn_{0.95}Mn_{0.05}O$ samples shows a decrease of the white-line intensity and a well defined peak at ~ 16 eV above the edge. This peak is not present in the spectrum reported in Ref. [25] nor in the theoretical calculation. The comparison of the experimental spectra with that of MnO_2 suggests that this peak is simply due to the presence of a small amount of MnO_2 in the samples, also in agreement with the white line reduction due to the diverse Mn environments.

4. Summary and Conclusions

We have performed an X-ray absorption spectroscopy study of $Zn_{0.95}Mn_{0.05}O$ thin films prepared with different sputtering gas and presenting room temperature ferromagnetic

Figure 8. (color online) a) Comparison between the experimental Mn K-edge XANES of Mn:ZnO (●) and computations performed by considering that Mn substitutes Zn in the wurtzite ZnO structure adapting the interatomic Mn-O distance in the first coordination shell. b) Comparison between the experimental Mn K-edge XANES spectra of Mn:ZnO-Wurtzite (●); Ar (blue, ○) and Ar/N₂ (red, open triangles) prepared Zn_{0.95}Mn_{0.05}O films and the theoretical computation performed by considering that Mn substitutes Zn in the wurtzite ZnO structure adapting a Mn-O interatomic distance of 2.09 Å in the first coordination shell (green, dots). The experimental spectrum of MnO₂ is also shown (green, open squares).

behaviour. The experimental data have been compared to *ab-initio* XANES computations performed at both the Zn and Mn K-edge within the multiple-scattering framework.

The comparison of the theoretical computations with the experimental data of the reference compounds MnO and ZnO, both in wurtzite and rocksalt structures, indicates the need of using large clusters to reproduce the experimental spectrum and, moreover, that the computations performed by using the Dirac-Hara (DH) exchange and correlation potential yields the best agreement with the experimental data. In this way, all the experimental spectral features and the relative energy separation among these features are well reproduced by the DH computations.

This computational scheme has been applied to the case of ZnO thin films doped with 5% at. Mn. Our results indicate that Mn substitutes Zn in the wurtzite structure. However, contrary to previous claims, the results of these computations indicate that by assuming a reliable defect concentration randomly distributed the presence of both oxygen and zinc vacancies is not detectable in the XANES spectra. Indeed, the theoretical computations presented here point out that Mn adapts its local environment by increasing the Mn-O interatomic distance with the nearest-neighbours oxygen atoms. This modification is slightly different for the $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ thin films prepared with different sputtering gas, which suggests that the different magnetic behaviour observed for the different samples is related to the different local structure of Mn in the films. This different magnetic behaviour might be also affected by the presence of MnO_2 traces detected by X-ray absorption spectroscopy. Therefore, these results give theoretical support to the previous works [16, 15] suggesting that the local order around Mn is of fundamental importance regarding the magnetic properties of the ZnMnO systems.

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7. Supplementary Information

Figure 9. (color online) Top panel: Comparison between the experimental Zn K-edge XANES of rocksalt ZnO (●) and the computations performed by using complex ECPs: HL (red, dashes) and *complex* DH (blue, solid line). Bottom panel: Comparison of the experimental Mn K-edge XANES spectrum of MnO and the computations performed by using real ECPs: DH (blue, solid line) and *real* HL (red, dashes).

Figure 10. (color online) Comparison between the experimental Mn K-edge XANES of Mn:ZnO (●) and computations performed by using HL ECP and by considering that Mn substitutes Zn in the wurtzite ZnO structure adapting the interatomic Mn-O distance in the first coordination shell.