

New XMCD study on thiol capped ZnO nanoparticles

J. Chaboy¹, M. A. Laguna-Marco², M. A. García³, C. Piquer¹, R. Boada¹

¹Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, ²Advanced Photon Source APS, Argonne National Laboratory, ³Instituto de Cerámica y Vidrio, CSIC.

Introduction:

One of the main goals of material science nowadays is the development of multifunctional materials combining properties that do not stand together in traditional materials. For instance, the coexistence of semiconductor properties (basis of the microprocessors) and room temperature ferromagnetism (as non volatile memories) in a single material will push the development of new and optoelectronic devices with higher reliability and lower power consumption [1,2]. In the last years the research for this kind of materials was focused on the so-called Diluted Magnetic Semiconductor (DMS), material consisting on a semiconductor matrix with a small amount of dispersed magnetic [3-4]. Despite some initial promising results [5], it is not clear if those materials are intrinsically ferromagnetic and nowadays the situation of DMS is confusing [6].

More recently, a significant number of experimental results pointed out the possibility to induce magnetism in non-traditional magnetic materials due to size and surface effects in nanostructures [7]. Most of these results appeared in oxides without any doping of magnetic atoms, but with modified electronic structure due to the presence of surface bonds [8,9]. Within this scenario it appears of paramount interest to deepen the study of systems which are not magnetic in the bulk and that by reducing size and inducing the alteration of its electronic structure, without introducing magnetic impurities, exhibit evidence of *exotic* magnetism. This is the case of ZnO nanoparticles capped with different organic molecules for which it has been recently shown [9] that it is possible to induce magnetic properties ranging from pure diamagnetism to the appearance of a ferromagnetic-like contribution without doping with magnetic impurities. These results were interpreted in terms of a correlation between the charge transfer produced by the surface bond and the magnetic moment, proposing that their magnetism is related to the modification of the electronic structure of the nanoparticles due to the bonds with the molecules. Since ZnO is a semiconductor widely used in spintronics applications, it is of fundamental interest to determine whether undoped ZnO can be ferromagnetic or not.

Experiment:

To this end we have performed XMCD measurements at the K-edge of Zn in ZnO nanoparticles capped with different molecules to establish the origin of their magnetic properties. A key point to understand this effect is to determine if the magnetic moment relays on the ZnO or in the molecule. If the observed magnetism is associated with the creation of oxygen 2p holes, the sp-band of Zn should be also concerned due to the hybridization. At this stage XMCD is the only magnetic measurement technique with the elements sensitivity required to elucidate this question.

Result and Discussion:

The result of such a measurement is reported in Fig.1. The existence of a non-zero Zn K-edge XMCD signal constitutes the first experimental demonstration of the magnetic polarization of the Zn atoms in these capped ZnO nanoparticles, which in its turn evidences the intrinsic nature of their magnetism.

The existence of the magnetic polarization of the Zn p-band does not depend on the capping agent. As shown in Fig. 1 similar Zn K-edge XMCD signals are detected in ZnO samples capped with Amine, Topo and Thiol. The main difference of the capping

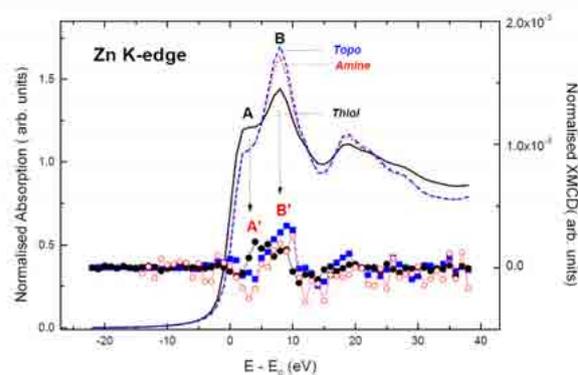


Fig.1 Comparison of the normalized Zn K-edge XMCD spectra recorded at $T = 4.2$ K and $H = 10$ T in the case of ZnO NPs capped with Amine (○), Topo (■) and Thiol (●). The comparison of the normalized XAS spectra is also shown: Amine (dots), Topo (dashes), Thiol (solid line).

molecules comes from the atom involved in the bond to the ZnO NPs, being N, O and S in the case of Amine, Topo and Thiol, respectively. Despite the magnitude of the XMCD signals is similar in the three cases, the shape of the XMCD spectra shows interesting differences. In particular, the spectrum of the thiol sample exhibit a significant variation of the main spectral features: the intensity of peak A enhances while that of peak B is significantly reduced. Similar results are found in the XMCD spectra: in the case of the thiol sample for which peak A' becomes positive, resembling to some extent the enhancement of the peak A intensity.

The modification of the XAS profile has been often accounted in terms of changes of the electronic structure. However, the modification of both the spectral shape and the intensity of the main absorption features is not only due to electronic because they are intimately linked to the local structure [10]. The magnitude of the observed differences between the Zn K-edge XAS spectra of the thiol-capped sample and those of the Amine and Topo ones suggests that structural effects have to be taken into account to understand the XAS behaviour. The bond of the surfactant molecule to the ZnO particle takes place at the surface. Therefore, we can distinguish two different Zn atoms contributing to the K-edge absorption, i.e. those at the bulk-like part of the particle and those at the surface in which new Zn-N or Zn-S bonds can exist depending of the capping.

We have performed a detailed ab-initio calculation of the Zn K-edge XAS aimed to determine the influence of the different coordination induced by the capping. We present in Fig. 2 the computations made for a small ZnO cluster containing the O and Zn coordination shells within

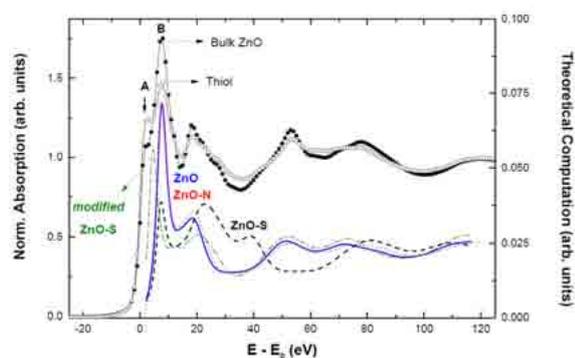


Fig.2 Comparison of the experimental Zn K-edge XANES spectra of bulk ZnO (●) and thiol-capped sample (○) and the theoretical spectra calculated for a ZnO cluster (solid line) and the same cluster in which the O neighbours have been substituted by N (dots) and S (dashes) at the same atomic position. The dotted-dashed line corresponds to a ZnO cluster in which S atoms substituting O have been placed at a greater interatomic distance.

the first 3.25 Å around absorbing Zn. Then, we have substituted the O atoms by N and S atoms at the same positions. The substitution of O by N has little influence in the XAS spectrum and only slight amplitude differences are detected beyond the main line. However, when S atoms are placed at the oxygen sites the computed spectrum completely changes and it does not resemble the experimental one. However, if we modified the Zn-S distance from 1.97 Å, corresponding to the Zn-O bond in ZnO, to 2.34 Å as found in the zinc blende, we observe that the computed spectrum becomes similar to those computed for the original and N-substituted ZnO clusters but shifted to lower energies. Interestingly, the main absorption line lies close to the A peak which is more intense in the case of thiolated samples.

These results suggest that in addition to a ZnO structure, there is an interface at the surface between the core of the particle and the capping molecule in which S substitutes O but accommodating the Zn-S interatomic distance as found in ZnS. Therefore, the observed modification of the XMCD spectra shown in Fig. 1 through the different capped NPs can be addressed to the formation of this interface.

Conclusion:

Summarizing, we have reported here evidence of the magnetic polarization of Zn atoms in ZnO nanoparticles capped with different materials. The XMCD experiments at the Zn K-edge show irrefutable evidence of magnetic polarization. The signal appears on ZnO NPs independently of the capping. The evolution of both XAS and XMCD signals as a function of the capping agent point out the formation of a well defined interface in which the Zn atoms bond to the atoms of the capping molecule. These data point out that the exotic magnetism of these capped ZnO nanoparticles resides at the hybridized p band formed among Zn and the bonding atom of the molecule.

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