

Report - 25 01 626

(Round 1, 12-16 July 2006)

Anomalous magnetic behaviour in FeCuZr amorphous alloys

In the first round of this experiment initially planned to perform measurements XANES and EXAFS measurements in FeCuZr amorphous alloys there was an experimental problem with the setup and measurements and it was only possible to measure at room temperature. As the planned experiments required the measurements at different temperatures (see proposal) we move to another topic that could be studied with the conditions of the available beam. Hence, we performed EXAFS and XANES measurements on ZnO nanoparticles in order to understand the magnetic properties of this system.

Magnetic semiconductors are nowadays of great interest in view of the potential application of those materials in the development of spintronic devices. In the last years, following the proposal by Ohno [1,2] the research on these magnetic semiconductors has been mainly focused on the so-called Diluted Magnetic Semiconductors (DMS): Semiconductors containing a small amount of magnetic impurities. The most recent and outstanding works on this field showed that the magnetic properties are not exclusively related to the presence of the magnetic ions but strongly determined by the alteration of the electronic structure of the semiconductor matrix (by doping it with p or n type defects) [3,4,5,6]. For instance, Kittilstved et al [3,4] showed that Mn:ZnO nanoparticles and thin films only show room temperature (RT) ferromagnetism when capped with molecules that introduce p-type defects, while other capping that introduce n-type defects leads to no RT ferromagnetism. On the contrary, for Co:ZnO films the n-type defects favours the appearance of RT ferromagnetism while p-type defects yield to no RT ferromagnetism. Moreover, Coey et al [5] demonstrated that doping ZnO

thin films with 3d non magnetic ions (as Ti or V) also leads to RT ferromagnetic behaviour and for insulating HfO_2 the effect appear even without doping [6]. Those results point on the alteration of the electronic structure of the semiconductor (induced by both, the presence of the magnetic impurity and the defects) as responsible of the origin of the observed magnetism.

We recently found that an alteration of the electronic structure of Au nanoparticles and thin films produced by capping them with organic molecules also lead to the appearance of RT ferromagnetism despite the diamagnetic character of bulk Au [7,8,9]. Thus, it is still to be elucidated if the effect found for Au surfaces (NPs and thin films) can also be present in semiconductors, that is, if an alteration of the electronic structure of the semiconductor by capping with certain molecules, can yield the appearance of RT ferromagnetic behaviour even in absence of magnetic ions.

In this work we experimentally show that capping ZnO NPs with a variety of organic molecules modifies its electronic structure arising ferromagnetic-like behaviour up to 300 K. Therefore, this method opens a new way to obtain the desired magnetic semiconductors without using any type of magnetic atoms and avoiding the superparamagnetic limit.

ZnO NPs with wurtzite structure and a narrow size distribution with $\langle D \rangle = 10$ nm (see figure 1) were prepared via sol-gel using the procedure described in [3] and capped with capped with three different organic molecules: Tryoctylphosphine (named after here TOPO), tryoclytamine (AMINE) and dodecanethiol (THIOL), which bond to the particle surface through an O, N and S atom, respectively. The size, shape and crystallographic structure of the particles resulted independent of the capping molecule.

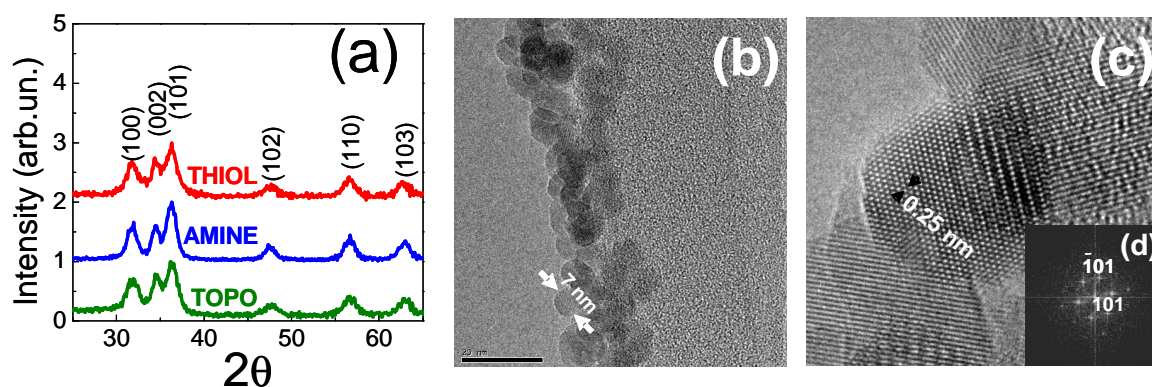


Figure 1. (a) X-Ray diffraction patterns of the AMINE, THIOL and TOPO samples: diffraction maxima (labelled) are indexed on the basis of a ZnO wurtzite type unit cell. (b) Low magnification image of the AMINE sample, showing the size distribution. (c) HREM image along [010] zone axis and (d) corresponding FFT in agreement to the wurtzite unit cell.

Figure 2 show the XANES spectra at the Zn K-edge measured at RT in the SPLINE (BM25) beamline at ESRF. The spectra are clearly different for the three capping molecules. The Zn K-edge, corresponding to the transition $Zn\ 1s \rightarrow 4p$, has been shown to be more sensible to the Zn chemical bonding than L edges. Although 4p level of Zn isolated atoms is empty, chemical bonding with different chemical species leads to hybridization, resulting states with a different degree of occupation depending on the features of the bond. In particular, a larger intensity at the first maximum is associated with a larger charge transfer between the Zn atoms and the surrounding atoms, that can be due to an increase of the coordination number or changes in the electronegativity of these surrounding atoms. Hence, variations in intensity at the first maximum indicate different degree of occupation for the outer orbital of Zn atoms (including the hybridized states) for the three samples.

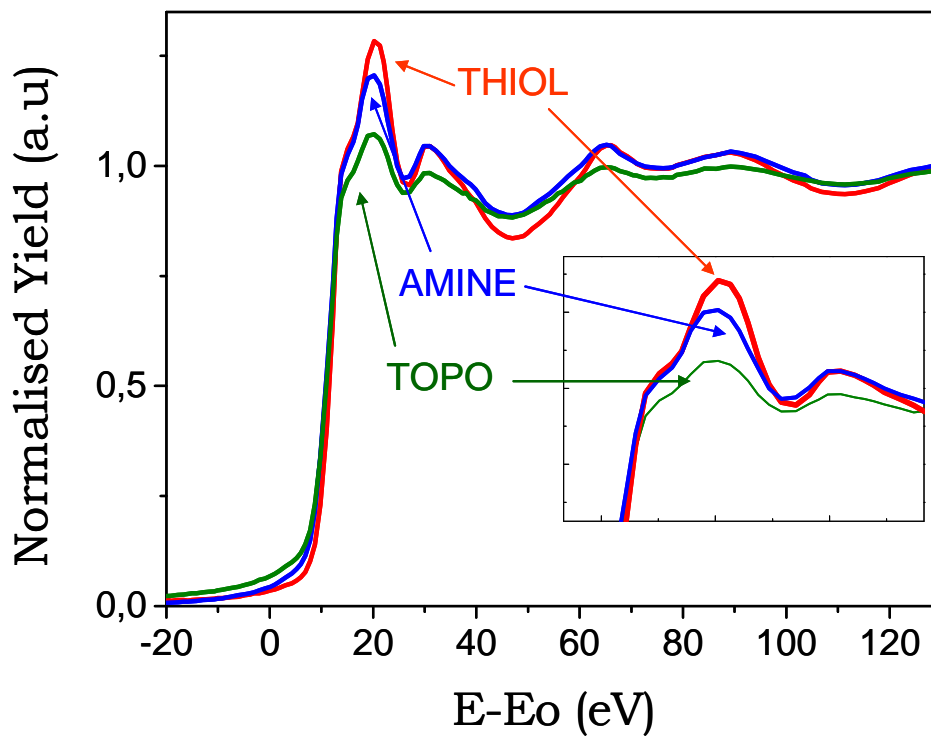


Figure 2 XANES spectra measured at the K-edge of the Zn for the three different organic molecules

The photoluminescence emission intensity at 550nm (Figure 3) which is ascribed to ZnO surface defects, results also different depending on the capping molecule, confirming that those molecules alter the electronic configuration of the particles in a different way.

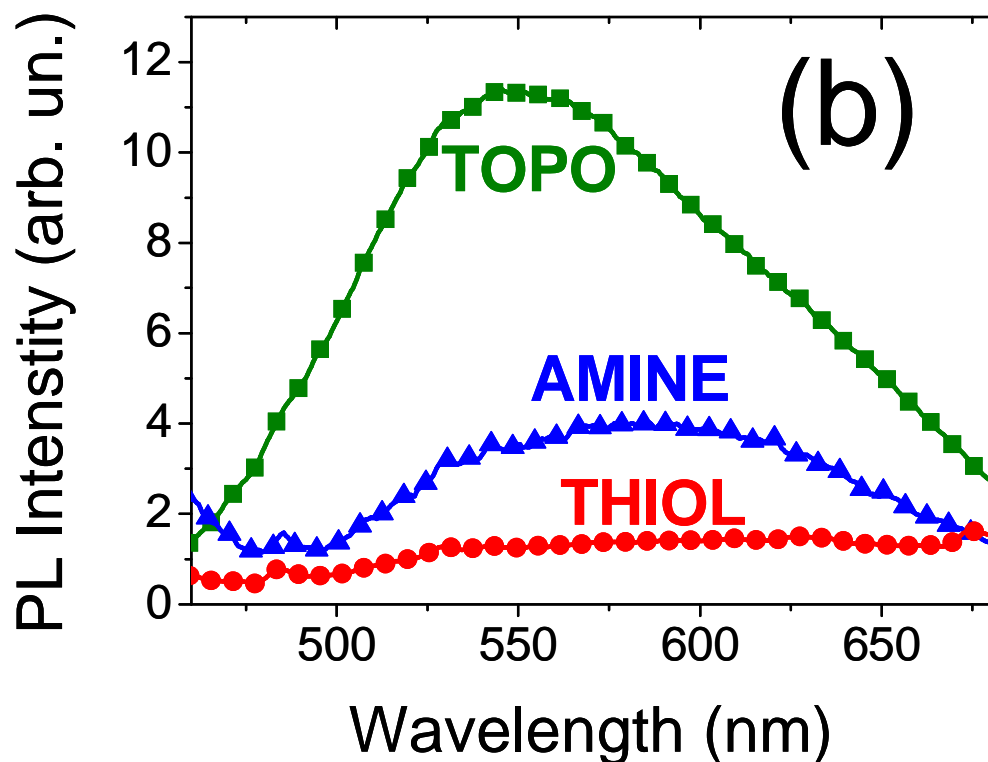


Figure 3. Photoluminescence emission spectra measured upon excitation with 385 nm light for the same samples.

Figure 4 show the magnetization curves of the samples at 300 K (identical results at 5K). The samples exhibit diamagnetic character as bulk ZnO does but for the AMINE and THIOL capped NPs there is a ferromagnetic-like contribution that can be clearly observed after subtracting the diamagnetic background. For an average nanoparticle size of 10 nm, the magnetic moment per surface atom resulted $2 \cdot 10^{-3} \mu_B$ and $0.5 \cdot 10^{-3} \mu_B$ for THIOL and AMINE sample respectively. These values are calculated assuming that no rests of the precursors are present in the sample; they represent therefore a lower limit.

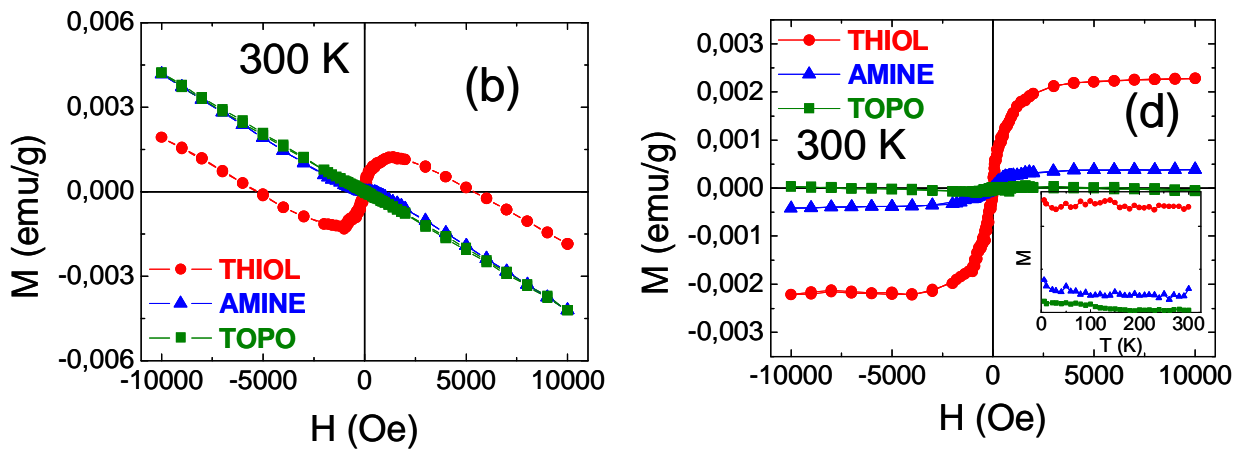


Figure 4. (left) Magnetization curves for the different samples and (right) the curves after subtracting the diamagnetic component.

It is worthy noting that structural analysis of the NPs showed about identical structure irrespective of the capping molecule but those measurements probing the electronic structure (XANES, PL and magnetic properties) confirmed that these are strongly dependent on the capping molecule. These results demonstrate that an alteration of the electronic structure of a semiconductor induced by doping it with defects (p or n type) or impurities can promote the appearance of magnetism. When the doping impurities are magnetic ions, they will introduce and additional contribution to the magnetization. Although these isolated magnetic impurities diluted in a non-magnetic matrix are expected to behave as paramagnetic (and rapidly decreasing with T), they could interact with the magnetism arising from the defects, amplifying or cancelling their effects, as shown for Mn and Co doped ZnO thin films doped type p or n [4].

Publications derived from the experiment

- **Magnetic properties of ZnO Nanoparticles.** M. A. Garcia, et al *Nano Letters* 7 (2007) 1489.

- This paper was highlighted in *Nature Materials* 6 (July 2007) 470.

-According to the ACS webpage it was the most accessed article of the trimester:

http://pubs.acs.org/journals/nalefd/promo/most/most_accessed/2007q2.html

Ferromagnetic behaviour in semiconductors: a new magnetism in search of spintronic materials. A. Quesada, M.A. García, J. de la Venta, E. Fernández Pinel, J.M. Merino, A. Hernando. *The Eur. Phys. Jour. B* 59 (2007) 457

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