



	<b>Experiment title:</b> X-ray microprobe in transition metal doped ZnO	<b>Experiment number:</b> MA229
<b>Beamline:</b> ID21	<b>Date of experiment:</b> from: 14/02/2007 to: 20/02/2007	<b>Date of report:</b> 24/08/2007
<b>Shifts:</b> 18	<b>Local contact(s):</b> Emilie CHALMIN	<i>Received at ESRF:</i>
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### Report:

A set of Mn doped ZnO samples deposited on nanoporous anodic alumina templates have been studied by means of scanning XRF and XANES at ID21 microprobe beamline. The purposes of the work were: to quantify the Mn content in the layer; to analyze the local arrangement of Mn in the ZnO host lattice; to clarify the existence of clusters; and to obtain the valence of the Mn atom. All these relevant factors that could contribute to clarify the origin of ferromagnetism with high Curie temperatures of diluted magnetic ZnO.

The typical XRF spectra of the ZnO samples with different Mn contents are shown in Fig. 1. The  $K\alpha$  and  $K\beta$  fluorescence lines of Mn and Zn, as well as those of Ar are shown in the spectra taken at 12 keV. The presence of residual atoms like Cu, Ni and Cr could play a key role in the resulting magnetism. The Mn concentrations, ranging from 2.2% up to about 9%, were estimated from the Mn and Zn  $K\alpha$  line intensity ratio using the PyMCA code. We have used  $\rho=5.8$  g/cm<sup>3</sup> for the ZnO density and  $d=0.5\pm 0.1$   $\mu$ m for the layer thickness in the calculations. Therefore, our results shows additional contamination mainly with heavy transition elements during the involved electrodeposition steps. In general, these impurities could affect both the incorporation and agglomeration stages of microdefect formation, being crucial particularly in the magnetic properties. It has been shown that uncompensated spins in antiferromagnetic nanoparticles could produce additional sizeable spontaneous magnetization at high temperatures.

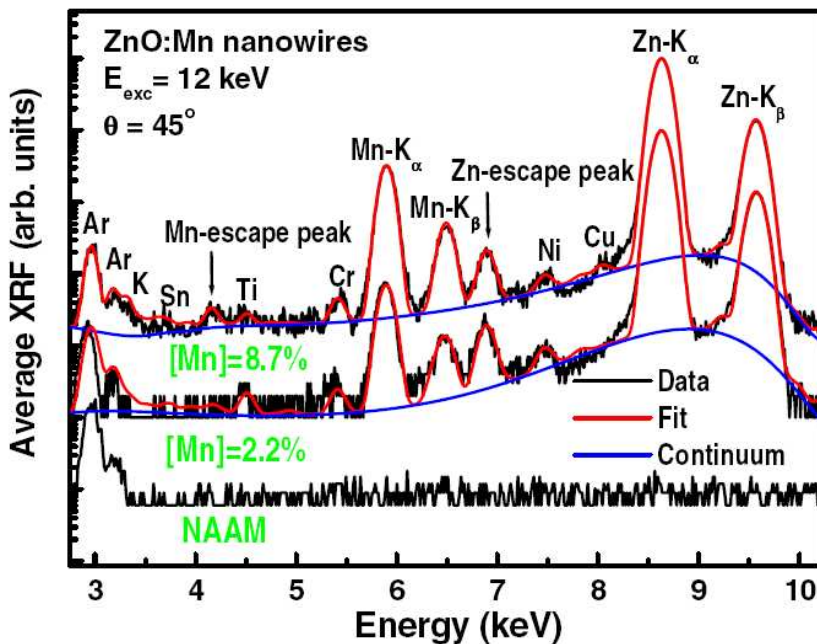


Fig. 1: XRF spectra of ZnO nanowires and anodic alumina template.

Then, by setting regions of interest around the dominant fluorescence lines, and taking advantage of the scanning microfluorescence technique at the ID21 beamline, the compositional homogeneity of all samples was also analyzed with micron spatial resolution. Elemental maps of Mn were obtained by measuring the Mn line intensity on the sample surface (see Fig. 2). The Mn patterns in both samples show striking spatial variations, indicating the cluster formation on the micrometer scale. The cluster density is about  $6 \times 10^{-2} \mu\text{m}^{-2}$  with  $1 \mu\text{m}^2$  size. The obtained patterns suggest surface segregation effects of Mn centers independent on the Mn content.

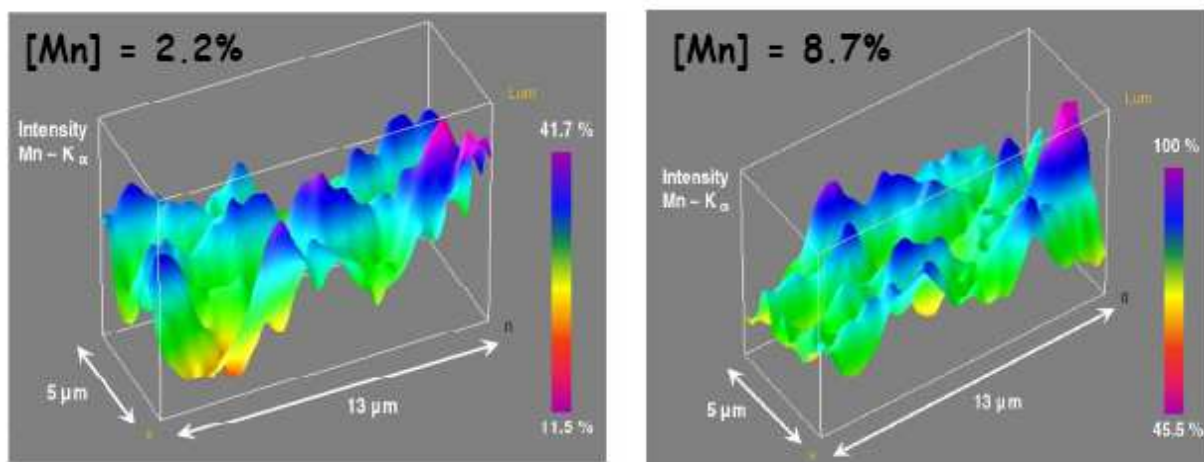
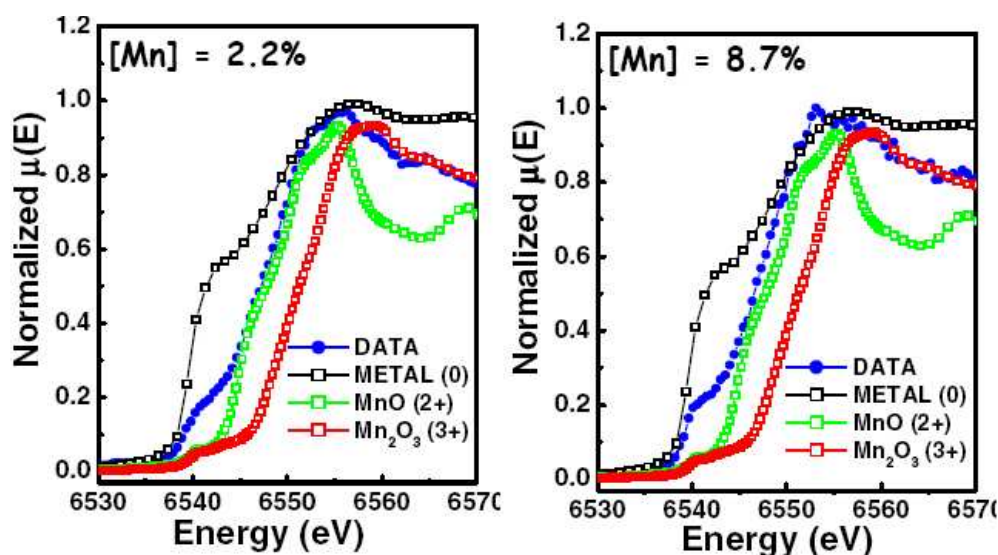


Fig. 2: XRF images of ZnO nanowires obtained by measuring the Mn line intensity over the sample surface.

Based on XANES spectra from other possible configurations (metallic Mn, MnO, or  $\text{Mn}_2\text{O}_3$ ), Figure 3 displays different Mn oxidation states. Although model compounds with local structures similar to the wurtzite ZnO crystal lattice is the ideal situation, only Mn oxides were available. The natural state of the Mn incorporated into the ZnO host material is one of the most relevant and significant issues today. This depends upon the crystal growth method, details of the Mn incorporation in the crystal, as well as the postgrowth process. In principle, when a Mn atom is introduced in a II-VI compound, it takes the metal site and its five electrons remain bound to  $d$  orbitals. A direct comparison to the XANES data reveals clear differences and also confirms predominant valence 2+ of Mn atoms in ZnO. The spectra from the samples have similar features, except slight differences on the relative peak intensities and preedge regions. Because dipole transitions dominate, the final state of the photoelectron will be of angular momentum  $l=1$  due to the dipole final state selection rule ( $\Delta l = \pm 1$ ). Thus, usually the large density of unfilled  $d$  states of transition metals does not contribute to a  $K$  edge. However, mixing of these  $d$  states with  $p$  character states from the surrounding atoms can occur without inversion symmetry, causing peaks below the steeply rising part of the edge. Generally, the substitutional incorporation of a transition metal increases linearly the intensity of this preedge peak,<sup>19</sup> showing a progressive participation of  $3d$  orbital in the bonding. However, in our measurements, the



relative intensity of the prepeak in the Mn  $K$  edge XANES spectrum, with respect to the white peak, remains constant, indicating that the Mn site configuration is the same independent of its concentration in the wurtzite lattice.

Fig.3: XANES spectra of ZnO nanowires near the Mn  $K$ -edge. For a direct comparison the spectra of several model compound have been included.