Report

HE 2118 - Room temperature ferromagnetism inthe Mn-Zn-O system

Diluted Magnetic Semiconductors (DMS) are one of the most active fields of research nowadays because of their potential applications in magneto-optical-electronics[1]. But these materials would be a major development only if their ferromagnetism (FM) is unambiguously established to be intrinsic (carrier-mediated), and if the Curie temperature of the system is above room temperature (RT). Since Dietl *et al.*[3] predicted that Mn-doped ZnO could be a DMS with a Curie temperature over 300 K, the study of the magnetic properties of this system has attracted a great deal of work, mainly marked by controversy. Following the first experimental observation of RT FM in this system in Mn:ZnO bulk samples[4] prepared by thermal treatments of MnO_2 and ZnO, Kundaliya *et al.* [5] claimed that the FM found was not attributable to a DMS but to a secondary $Zn_xMn_{2-x}O_{3-y}$ phase. Moreover, Lawes *et al.*[6] found no ferromagnetism down to 2 K in bulk samples prepared by chemical methods. We recently demonstrated that the ferromagnetism appears when the reaction between ZnO and MnO_2 is partial leading to the coexistence of MnO_2 (with Mn^{4+}) and $ZnMnO_4$ (with Mn^{3+}) as figure 1 illustrates and we attributed the FM observed to the double-exchange mechanism taking place between Mn^{3+} and Mn^{4+} ions[7] located in the interfaces between both phases.

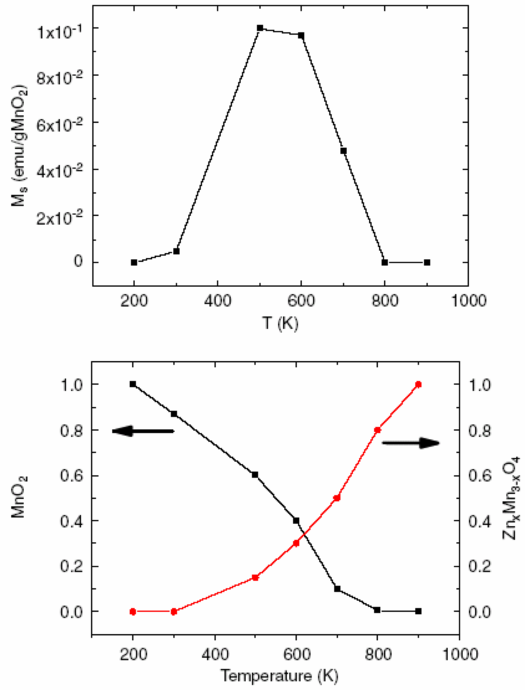

Figure 1. (top) Ms of ZnO-MnO_2 samples as a function of the annealing temperature and (bottom) abundance of MnO_2 and $ZnMnO_4$.

The aim of the experiment was to study the oxidizing state of the Mn atoms by XANES and its relation with the magnetic properties, as well as the polarization and its contribution to the magnetization directly by XMCD measurements on the K-edge of Mn.

2%MnO_2-98%ZnO pellets were prepared following the method described by Sharma *et al.*[4,8]. A first set of pellets was prepared using as-cast ZnO and MnO_2, a second one was made using ZnO after having calcined it at 950 °C for 8 hours. In a first step the samples were annealed at 500 °C for 30 minutes and 12 hours. On a second step they were exposed to thermal treatments at 700 °C and 800 °C for 12 hours. A single phase sample of the pure $ZnMn_2O_4$ spinel was prepared for comparison purposes by mixing the stochiometric proportion of MnO_2 and ZnO and annealing it at 900 °C. XANES measurement where preformed for selected samples.

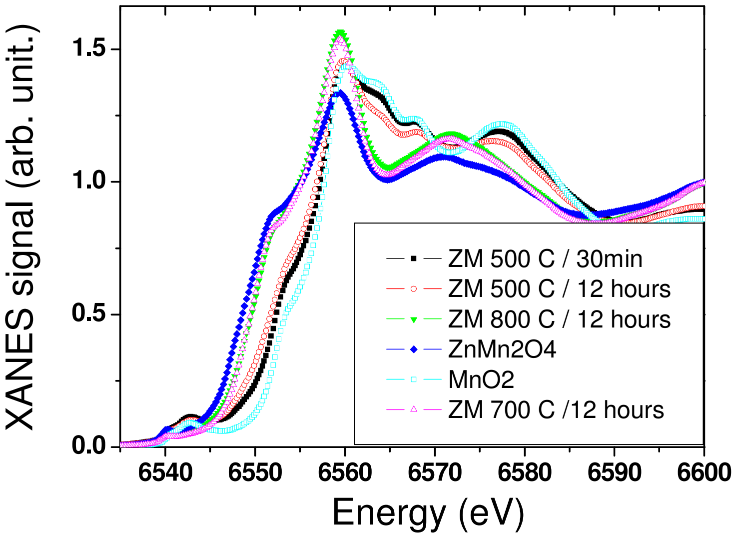

Figure 2. XANES spectra of several samples obtained at RT in the Mn K-edge.

As can be noticed in figure 2, the absorption edges of the ZM samples appear to be between the absorption edges of MnO_2 and $ZnMn_2O_4$. This fact indicates that in the ZM compounds the mean oxidation state of Mn atoms is between 3+ and 4+, and thus, that the two oxidation states coexist. The second inflection point at the edge position of the XANES spectra allows us to determine the energy shift of the edge relative to the reference compounds. Using the method described by Wong et al. for vanadium in vanadium oxides[10], the average oxidation state of Mn can be quantitatively determined. In oxides, bound electronic transitions exhibit a linear relationship between their energy positions and formal oxidation state. MnO_2 and $ZnMn_2O_4$ were employed to determine the energy shift of the absorption K-edge for Mn^{3+} and Mn^{4+}. The obtained mean oxidation state of Mn in each sample is shown in figure 3.

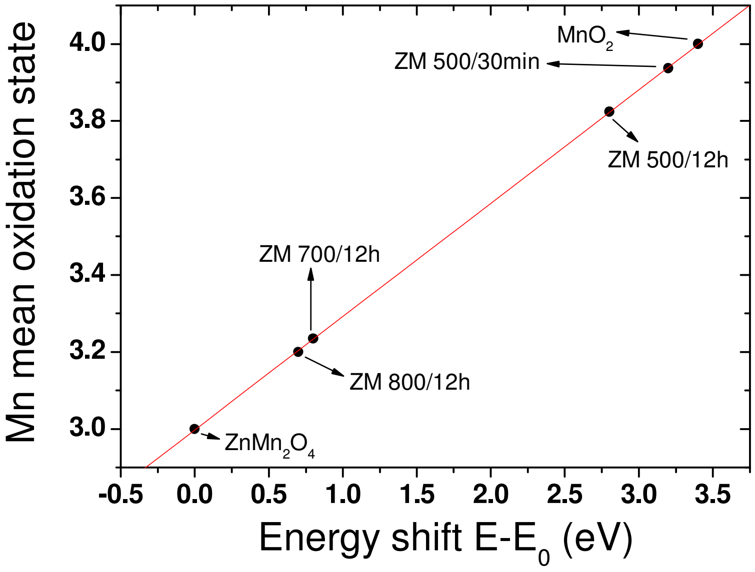

Figure 3. Oxidation state determination by the Mn K-edge energy shift of the samples.

The XMCD measurement could not be performed because of the dilution problem. As stated previously, only a few Mn atoms are in the interfaces where Mn^{3+} and Mn^{4+} coexists while most of them are in the bulk, MnO_2 or $ZnMnO_4$, so only a small fraction of Mn atoms are ferromagnetic making difficult to identify it by XMCD.

In summary, the XANES measurements in combination with conventional magnetometry (VSM), TEM, Raman spectra and XRD allows us to experimentally shon that Mn^{4+} and Mn^{3+} coexist in bulk ferromagnetic Mn-Zn-O. FM appears when only a small fraction of Mn^{4+} has reduced to Mn^{3+}, confirminging our previous proposal of double exchange a responsible of the RT fM observed in this system.

Additional measurements on the FeCuZr system

As the XMCD experiments could not be performed we have some remaining time we devoted to perform preliminary measurements on the FeCuZr system. The origin of the complex magnetic properties of iron rich metallic glasses containing low concentrations of early transition metals (Zr,Sc,Hf,Y) have attracted considerable interest during more than two decades, giving rise to several controversial microscopic interpretations.

We are studying the magnetic properties of amorphous and polycrystalline alloys $(Fe_{50}Cu_{50})_{100-x}$ Zrx obtained by ball-milling. This material shows an anomalous magnetic behaviour with the temperature, as observed in figure 4. The increase of the thermorremanence at temperatures over Tc has been previously related invar effect. As the samples are powder and amorphous, the typical measuring methods to study the thermal expansion can not be used in this case.

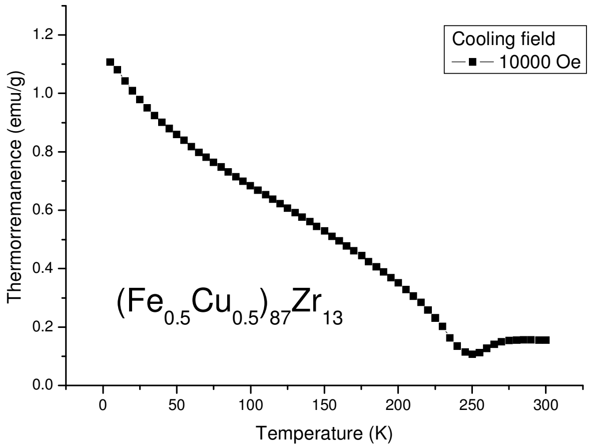

Figure 4. Thermoremanence measure performed for H=1T

From magnetic measurements performed at low temperatures and under an applied field of 5T, we have estimated the average magnetic moment of Fe atoms by assuming that Cu and Zr are not contributing to the magnetization. It is observed that:

i) Although fcc-Fe and fcc-Cu are not magnetic at their ground state, fcc-FeCu alloys exhibit ferromagnetic ordering and Fe atoms have a magnetic moment very close to that of Fe. This behaviour is not well understood and could be related with a magnetovolumen effect, since the lattice is expanded with respect to fcc-Cu or to a contribution to magnetization arising from Cu atoms.

ii) Upon Zr addition, the magnetic moment of Fe at 5T drops to values close to that of FerichZr alloys. A similar trend is observed for the Curie temperature, as observed in figure 2. However, it is observed that this value is much higher than that obtained through Mössbauer spectroscopy, as observed in figure 3.

iii) Low velocity Mössbauer spectroscopy shows that the isomer shift values decreases with respect to that FeCu alloys, indicating a charge transfer from Cu or Zr atoms to Fe, decreasing the magnetic moment. However the nature of the magnetic structure that could give rise to the observed behaviour remains obscure. It is expected that XMCD would help clarify this point, as observed in figure 3.

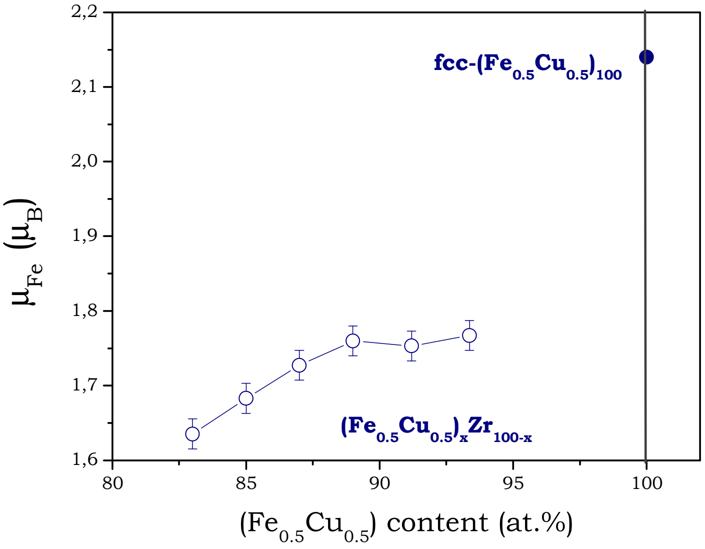

Figure 2. Magnetic moment versus concentration

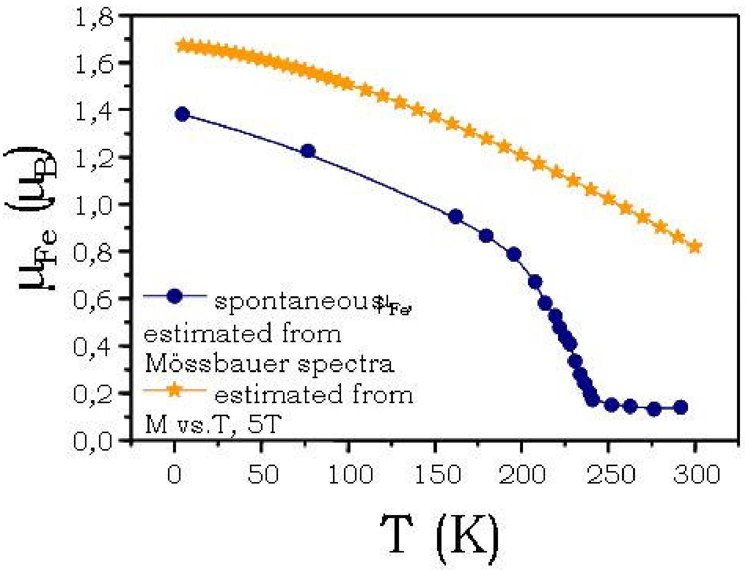

Figure 3. Comparison between the magnetic moment obtained from 5T Squid measurements and from Mössbauer spectroscopy

Finally, we would like to remark that a preliminary measurement of XMCD (figure 4) and histeresis loop (figure 5), obtained in ID12 of ESRF performed at 6T and 5K, see figure 4, measured at Cu K-edge, which is not the best energy for the characterization of possible magnetic moments of Cu but was the only energy available for try, seems to indicate that Cu atoms are polarized at low temperature.

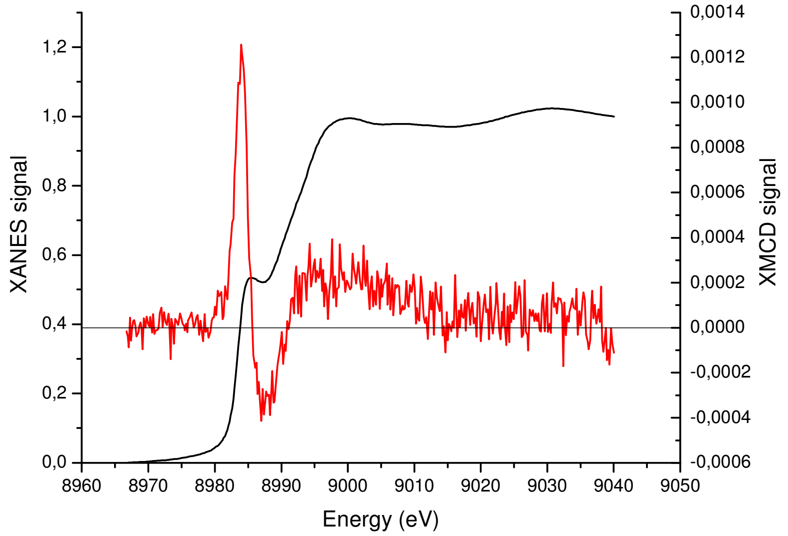

Figure 4. XMCD signal obtained on Cu K-edge

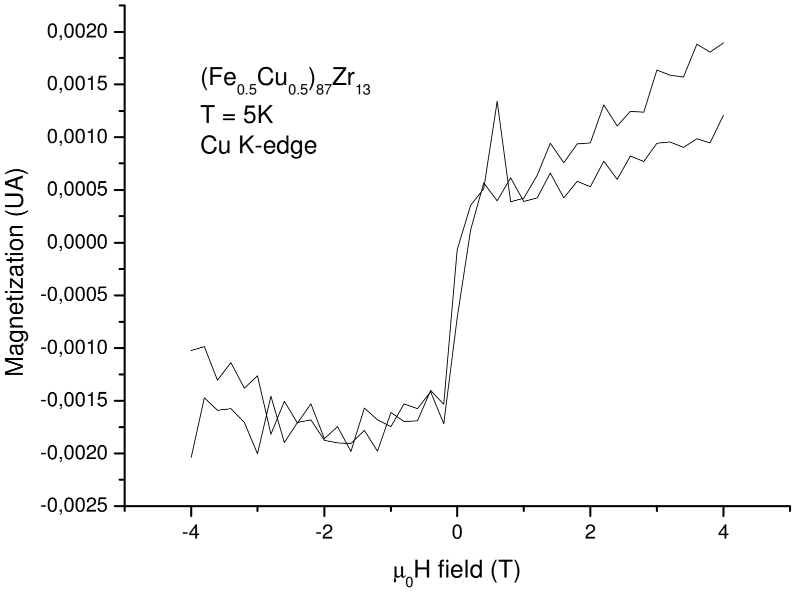

Figure 5: Magnetization curve obtained on Cu K-edge

This effect must be considered when analyzing the magnetic properties of this material and previous explanations must be revisited in view of this result and further XMCD experiments on this system.

Publications derived form the experiment

A. Quesada et al, *Experimental evidence of double-exchange contribution to ferromagnetism in Mn-Zn-O: A XANES analysis.* submitted to Phys. Rev. Lett. (CODE LH11644)

References

[1] H. Ohno, Science 281, 951 (1998).

[2] H. Munekata et al., Phys. Rev. Lett. 63, 1849 (1989).

[3] H. Ohno, H. Munekata, T. Penney, S.vonMolnar, and L.L. Chang, Phys. Rev. Lett. 68, 2664 (1992).

[4] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science 287, 1019 (2000).

[5] P. Sharma et al., Nat. Mater. 2, 673 (2003).

[6] D. Kundaliya et al., Nat. Mater. 3, 709 (2004).

[7] G. Lawes, A.S. Risbud, A. P. Ramírez, and R. Seshadri, Phys. Rev. B 71, 045201 (2005).

[8] M.A. García et al., Phys. Rev. Lett. 94, 217206 (2005).