ROOM TEMPERATURE FERROMAGNETISM IN THE Mn-Zn-O SYSTEM: A NEW INTERPHASE MAGNETISM

M. A. García[1,2], J. L. Costa-Krämer[3], J. F. Fernández[4], A. Quesada[1,2], M. L. Ruiz-González[5], M. A. Bañares[6], A. Wennberg[3], A. C. Caballero[4], M. S. Martín-González[3], M. Villegas[5], F. Briones[3], J. M. González-Calbet[1,5], and A. Hernando[1,2],

[1] Instituto de Magnetismo Aplicado (RENFE-UCM-CSIC), P.O. Box 155, 28230 Las Rozas, Madrid, Spain.
[2] Depto. Física de Materiales, UCM, 28040 Madrid, Spain.
[3] Instituto de Microelectrónica de Madrid, CNM-CSIC, Isaac Newton 8 PTM, 28760 Tres Cantos, Madrid, Spain.
[4] Instituto de Cerámica y Vidrio, CSIC, Cantoblanco 28049 Madrid, Spain.
[5] Depto. de Química Inorgánica I, UCM, 28040 Madrid, Spain.
[6] Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco; 28049-Madrid, Spain.

miguelag@renfe.esT

In the last years, there has been an increasing interest for magnetic semiconductors because of the enormous potential applications of those materials in the development of spintronic devices The first experimental observation of room temperature (RT) ferromagnetism (FM) was reported by Sharma et al [1] in low Mn content (10%MnO_2-90%ZnO and 2%MnO_2-98%ZnO) pellets annealed at 500ºC. The ferromagnetic behaviour was first explained in terms of the formation of Mn-doped ZnO, which was previously predicted to be a dilute magnetic semiconductor with a Curie temperature above 300 K [2]. However, the origin of the reported ferromagnetic behaviour is still a matter of controversy. Kundaliya et al [3], based on TGA experiments, suggested an oxygen-vacancy $Mn_{2-x}Zn_xO_{3-\delta}$ phase as responsible for the observed RT FM. Moreover, recent studies evidenced the absence of magnetic order in Mn-doped ZnO down to 2 K [4,5]. In recent works [6,7], we showed that the ferromagnetism is associated to the coexistence of Mn^{+3} and Mn^{+4} via a double exchange mechanism.

We prepared 2%MnO_2-98%ZnO and 10%MnO_2-90%ZnO pellets following the method described by Sharma et al [1]. Although we could reproduce the magnetic properties described previously, we found that samples were inhomogeneous (see figure 1). After annealing at 500ºC only a weak diffusion of Zn into MnO_2 grains was observed (while no Mn was found in the ZnO grains) leading to a partial reduction of $MnO_2 \rightarrow Mn_2O_3$ and the formation of $Zn_xMn_{3-x}O_4$. Annealing at higher temperatures increases the presence of this latter phase and simultaneous reduction of the ferromagnetic signal.

Thermogravimetric analysis and Raman spectroscopy confirmed the coexistence of Mn^{+3} and Mn^{+4}. Coexistence of both Mn oxidation states is known to be responsible for FM via double-exchange mechanism in different compounds [8,9] that usually exhibits large Curie temperature (T_C), even above RT [10]. The presence of Zn seems to favour the reduction at low temperatures, therefore, it is expected that both Mn^{3+} and Mn^{4+} coexist in the interface which separates regions with Zn from those without Zn, that is, the Zn diffusion front into Mn oxide grains. Figure 2a summarises the situation.

In order to confirm this point, we have tried to increase the MnO_2/ZnO interface (and therefore the surface of the Zn diffusion front) by growing a thin film multilayer sample consisting of 40 sequential ZnO/MnO_2 bilayers by pulsed laser deposition onto a Si substrate. The ZnO and MnO_2 individual layers are 7.5 and 1.5 nm thick respectively. The hysteresis

loops of this sample are shown in figure 2b. The saturation magnetization is 1 emu/cm^3, two orders of magnitude larger than the highest M_s reported for this system in bulk, and similar to the best value reported for thin films [11], confirming that the FM is originated at the interface.

Figures:

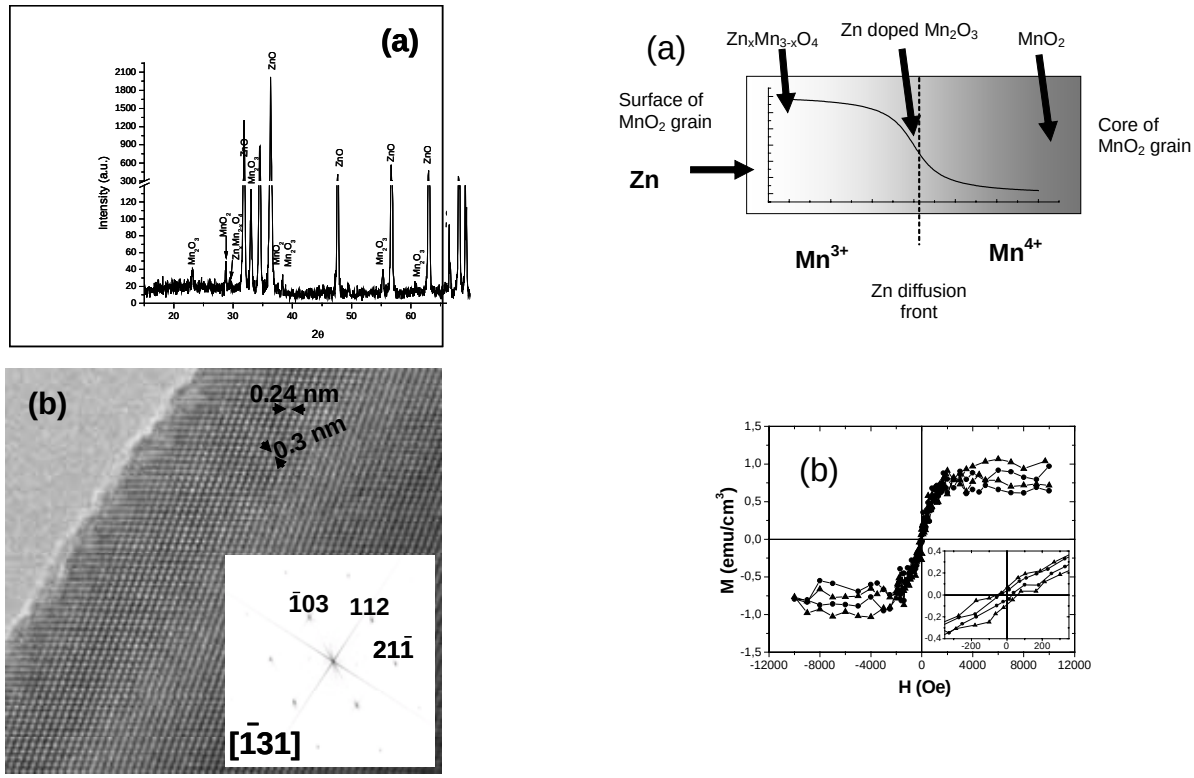

FIG. 2: (a) Scheme of the different phases at the Mn oxide grains after annealing at 500ºC and the oxidising states of Mn. The graph indicates the concentration profile of Zn inside the grain. (b) Hysteresis loops from a 40 MnO_2/ZnO multilayer prepared by laser ablation at 5K (triangles) and 300 K (circles). Inset shows a detail of the loops at low H. The paramagnetic/diamagnetic component has been subtracted to clearly show the FM phase.

References:

[1] P. Sharma et al, Nature Materials **2**, 673 (2003).
[2] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Science **287**, 1019 (2000).
[3] D. Kundaliya et al, Nature Materials **3**, 709 (2004).
[4] G. Lawes, A. S. Risbud, A. P. Ramírez, R. Seshadri, Phys. Rev. B **71**, 045201 (2005).
[5] C. N. R. Rao, F. L. Deepak, J. Mater. Chem. **15,** 573 (2005).
[6]J. L .Costa-Krämer et al, Nanotechn. **16** (2005) 214..
[7] M A. Garcia et al, submitted to Phys. Rev. Lett.
[8] M. B. Salamon, M. Jaime, Rev. Mod. Phys. **73**, 583 (2001).
[9] J. Alonso et al, Phys. Rev. B **64**, 172410 (2005).
[10] T. Okuda et al, Phys. Rev. Lett. **81**, 3203 (1998).
[11] N. Theodoropoulou et al., cond-mat/0408294.