

## Superficial room temperature magnetism in the ZnO:Co<sub>3</sub>O<sub>4</sub> system

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The discovery and understanding of room temperature ferromagnetic semiconductors (DMS) is proving to be a grand challenge in material science, since they would be excellent candidates to be used in the next generation of spintronic devices.<sup>i-iii</sup> Indeed, the question “is it possible to create magnetic semiconductors that work at room temperature?” is one of the 125 critical unanswered scientific enquiries recently propounded in *Science*<sup>iv</sup>. According to the theoretical predictions<sup>v,vi</sup>, doping certain semiconductors, such as ZnO, with a few transition metal atoms like Mn or Co would lead to this type of behavior. Although, the mixtures of ZnO with Mn and Co oxides exhibit room temperature magnetism (RTM) extensive doubts are still related with the origin and interaction between magnetic and semiconducting properties.

Nowadays, three different currents devoted to determine the origin of the magnetism and its relation with the semiconducting properties are found in the literature. a) One due to the doping of the transition metals like Mn or Co inside the ZnO lattice.<sup>vii,viii</sup> This makes conduction electrons become spin-polarized, so these materials are, in fact, magnetic semiconductors and for that useful for spintronic applications. b) A second current, in which the magnetism is explained to be due not only to the presence of magnetic ions, but also to the presence of ZnO oxygen defects.<sup>ix-xi</sup> And, c) a third one, in which those materials are not DMS and the magnetism is shown to be due to a secondary phase<sup>xii</sup> or we have attributed it before in the case of ZnO:MnO<sub>2</sub><sup>xiii</sup> to an interfacial double-exchange mechanism at the interphases of the diffusion front of Zn inside the MnO<sub>2</sub> particles.

In the present work, we concentrate on the reasons why mixtures of ZnO and Co<sub>3</sub>O<sub>4</sub> without thermal treatment present room temperature magnetic behavior, see figure I for the three different ratios employed in these studies. In addition, we try to explain why the RT magnetism of the material is related with a new type of interfacial magnetism.

In our case, the magnetism can be explained due to the distortion of a few nanometers of the surface of the Co<sub>3</sub>O<sub>4</sub> *during the mixing procedure* as detected by XPS and RAMAN. The annealing of these mixtures at low temperatures produced the diffusion of Zn into the Co<sub>3</sub>O<sub>4</sub> lattice, which reduced the magnetism in the samples. When Co-doped ZnO samples are observed (annealing temperatures up to 800°C) the ceramic powder presents no magnetic response.

This work was financed by CSIC (PIF) under MAGIN-CER project and by the SANDIE Network of excellence (Contract n° NMP4-CT-2004-500101 group TEP-0120). MSMG thanks to the Ramón y Cajal program.

## Figures

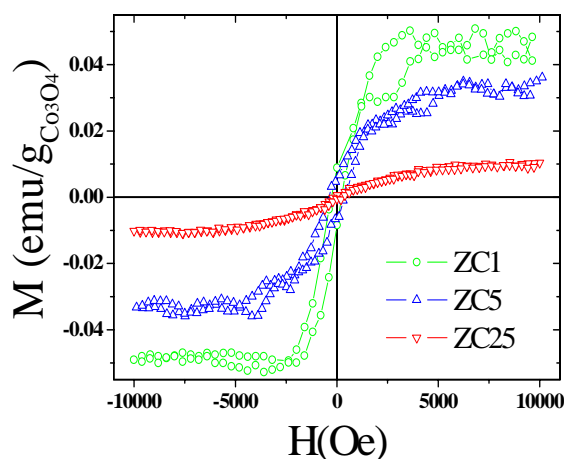


Figure 1. Magnetization curves at RT of the milled samples before any thermal treatment.

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