

Insights into the room temperature magnetism of ZnO/Co₃O₄ mixtures

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The origin of room temperature (RT) ferromagneticlike behavior in ZnO-based diluted magnetic semiconductors is still an unclear topic. The present work concentrates on the appearance of RT magnetic moments in just mixed ZnO/Co₃O₄ mixtures without thermal treatment. In this study, it is shown that the magnetism seems to be related to surface reduction of the Co₃O₄ nanoparticles, in which, an antiferromagnetic Co₃O₄ nanoparticle (core) is surrounded by a CoO-like shell. This singular superficial magnetism has also been found in other mixtures with semiconductors such as TiO₂ and insulators such as Al₂O₃. © 2008 American Institute of Physics.

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INTRODUCTION

The discovery and understanding of room temperature ferromagnetic semiconductors based on dilute magnetic semiconductors (DMS) is a grand challenge in material science, since they would be excellent candidates to be used in the next generation of spintronic devices.^{1,2} According to the theoretical predictions,³ doping certain semiconductors, such as ZnO, with a few transition metal atoms such as Mn or Co would lead to this type of behavior. Although the mixtures of ZnO with Mn and Co oxides exhibit room temperature ferromagnetism (RTFM), extensive doubts persist about the origin and interaction between magnetic and semiconducting properties.⁴ Nowadays, there are three different approaches in literature devoted to determine the origin of magnetism and its relation with the semiconducting properties. The first one is related to the doping of the transition metals such as Mn or Co inside the ZnO lattice,^{5,6} where conduction electrons become spin polarized, so these materials are, in fact, magnetic semiconductors and, for that, useful for spintronic applications. The second approach is where the magnetism is explained to be due not only to the presence of magnetic ions, but also to the presence of ZnO oxygen defects.⁷⁻⁹ The third one is where new discoveries point toward a different direction. These materials are not DMS and the magnetism is shown to be due either to a secondary phase¹⁰ or to an interfacial double-exchange mechanism at the diffusion front of Zn cations inside the MnO₂ particles, as we reported¹¹ for the case of ZnO:MnO₂.

Recently, just mixed ZnO:Co₃O₄ nanopowders without further thermal treatment show a well-defined hysteresis loops at 300 K,¹² which is indicative of a robust high temperature magnetic behavior, as compared with pure ZnO and Co₃O₄ which showed no RTFM. As it was observed, the

magnetic signals of the ZnO:Co₃O₄ mixtures were low enough to associate their origin to magnetic impurities; however, M_s decreases when increasing the Co concentration in the samples and with the thermal treatment at 400 °C and became nonmagnetic for thermal treatment up to 800 °C, thus, other possible mechanisms could not be discarded. Due to the importance of the appearance of RT magnetic behavior just by mixing ZnO with Co₃O₄, this study focuses in depth on this point. In addition, a study of the Co₃O₄ mixtures with other oxides with insulating properties demonstrates that this phenomenon is not only related with ZnO.

EXPERIMENTAL SECTION

ZnO:Co₃O₄ samples with ratios of (a) 99% ZnO, 1% Co₃O₄, (b) 95% ZnO, 5% Co₃O₄, and (c) 75% ZnO, 25% Co₃O₄ (named ZC1, ZC5, and ZC25, respectively, from now on) were fabricated following the low temperature procedure described previously:^{12,13} high purity (>99.9% Aldrich) ZnO with average particle size of 500 nm and Co₃O₄ nanoparticles raw powders were used for sample preparation. Also, nonmixed samples were prepared in the same conditions for comparison purposes. In addition, 1% Co₃O₄ mixtures with TiO₂ and Al₂O₃ were also prepared following the above-mentioned procedure. The average particle size was selected to be similar to ZnO.

The structural characterizations were carried out with a Siemens D5000 x-ray diffractometer. High-resolution transmission electron microscopy (HRTEM) was performed in a JEOL JEM 3000F. Charge to mass ratio is measured with a “Faraday cage” consisted in a double metal enclosure that were electrically isolated and the induced charge measured of the dried samples was measured with a Keithley high resistance electrometer model 6517A. X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 200R spectrometer provided with an AlK α x-ray source (1486.6 eV). Raman spectra were collected on a Renishaw micro-Raman system 1000. The samples were excited with

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the 514 nm Ar line. Magnetic properties were measured in a high temperature vibrating sample magnetometer above RT.

RESULTS AND DISCUSSION

In all of the samples mixed at RT, the presence of Co_3O_4 and ZnO was determined by x-ray diffraction (XRD). No displacement in the XRD peak positions were detected and no additional peaks related with other Co/Zn oxides were found. Therefore, at this scale, a reaction of components were not identified by XRD. Nevertheless, these mixtures present room temperature magnetic behavior while pure ZnO and Co_3O_4 do not.¹² In order to understand this change in the magnetic properties, a more in detailed study was performed.

The ZnO and the Co_3O_4 particles agglomerates as observed by TEM [Fig. 1(a)] and they stick together even after 1.5 h of ultrasonic treatment. This stickiness can be explained by the different superficial charge of the starting powders, which is -0.44 nC/g for ZnO and $+0.22$ nC/g for Co_3O_4 , as measured in a Faraday cage.

Pure ZnO and Co_3O_4 nanoparticles are found by HRTEM. The images show ordered structures. The planar distances of the ZnO particles correspond to pure wurtzite structure although energy dispersive spectroscopy (EDS) find a small amount of Co (around 1%). This apparent doping is not probably and appears related to the nearness of cobalt nanoparticles that would contribute to the x-rays signal recorded. The Co_3O_4 nanoparticles present a cubic spinel structure which belongs to the space group ($Fd3m$) and cell parameters of 8.0837 Å [Fig. 1(b)]. In which, Co^{2+} is in tetrahedral and Co^{3+} is in octahedral coordination. In case of the cobalt oxide nanoparticles, the EDS composition of the particles is around 99% Co and 1% Zn that reflects the above-mentioned detection limit. Nevertheless for these particles, if doping occurs, the cell parameters should not change since Co_3O_4 and ZnCo_2O_4 are isostructural with a very close unit cell. The presence of Co metal or other cobalt oxides can be excluded. Therefore, the magnetic properties of the mixture are attributed to the Co_3O_4 or ZnO particles, rather than to ferromagnetic impurity or the exchange coupling between Co metal and Co_3O_4 .

Since the previous techniques did not give an explanation to the magnetic response observed, a further study of the structural changes in Co_3O_4 and ZnO particles was performed by XPS, see Fig. 2. Pure Co_3O_4 spectra is characterized by a Co $2p_{3/2}$ peak at 780.2 eV a shake-up satellite peak at 789.3 eV, a Co $2p_{1/2}$ peak at 795.6 eV and the satellite at 804.8 eV. The separation among the spin-orbit component (15.4 eV), the satellites shape and its positions correspond with pure Co_3O_4 .¹⁴ In the case of ZnO: Co_3O_4 mixtures, no big changes are observed either in the $2p_{3/2}$, $2p_{1/2}$ peak positions or in the separation between them. This means that particles are essentially pure Co_3O_4 and no in diffusion of Zn into Co_3O_4 particles is detected. It should also be noted that the binding energies of these peaks are largely independent of the Zn:Co ratio, which also suggests that the local electronic structure of the cobalt oxides does not change with the compositions and emphasized that no Zn doping is produced.

However, important changes are detected in the satellite

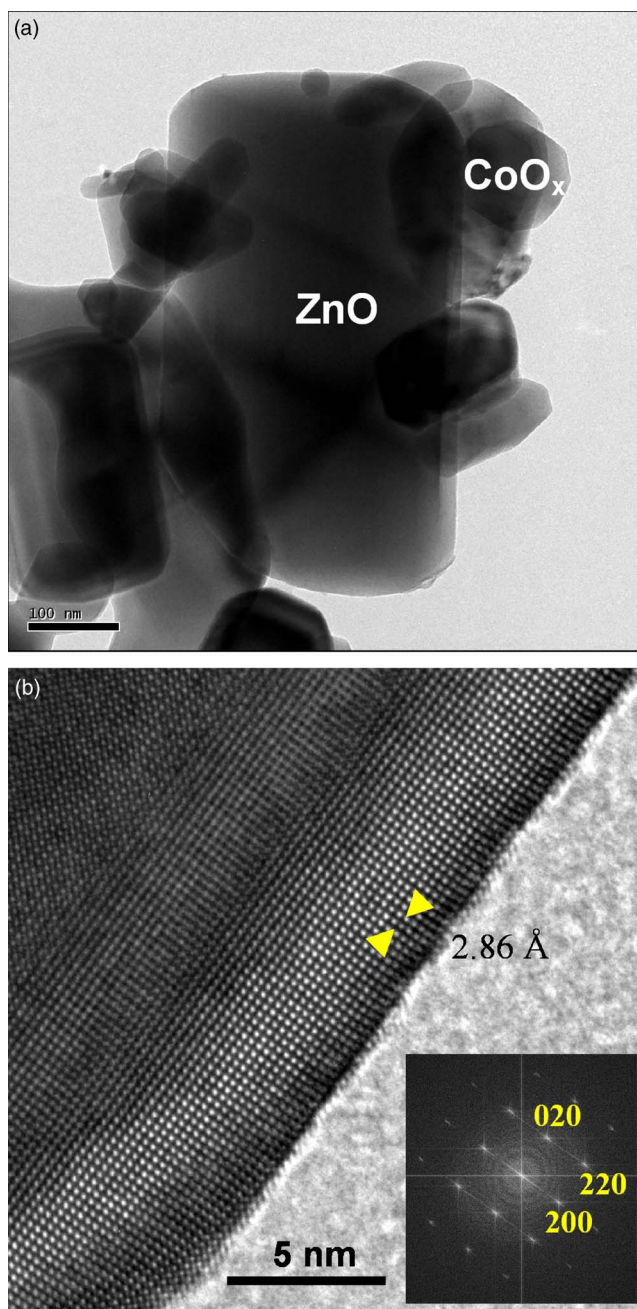


FIG. 1. (Color online) HRTEM of ZnO: Co_3O_4 mixture. (a) Low magnification shows the interaction between ZnO and Co_3O_4 particles and (b) high magnification of a Co_3O_4 particle on the [001] zone axis. (Inset) resultant FFT corresponding with a spinel structure.

peaks. They became more intense and appear at lower binding energies (785 and 803.5 eV). This position is representative of octahedral coordinated Co^{2+} , cations similar to those present in the CoO structure. The fact that the positions of the spin-orbit components remain unchanged and the satellites become more similar to CoO structure has been assigned before to Co_3O_4 with CoO-like structure at the surface.¹⁵ This means that some kind of reduction at the surface level is taking place just by mixing Co_3O_4 and ZnO in an attrition miller in water with zirconia balls. This agrees with the HRTEM and the XRD results, since the bulk of the particles is Co_3O_4 and only a few Co^{3+} ions (in octahedral coordination) of the surface are reduced to Co^{2+} . It is also

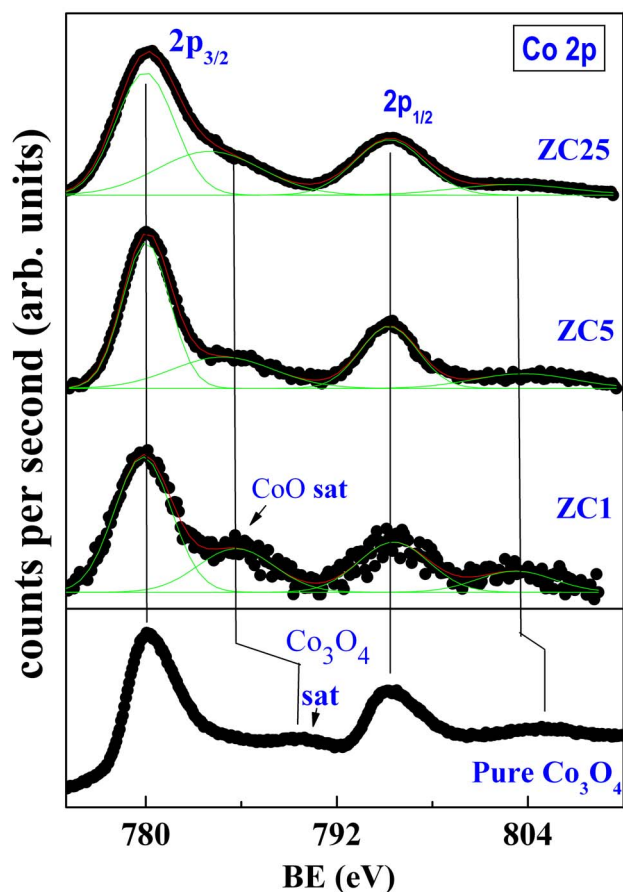


FIG. 2. (Color online) Photoemission spectroscopy of Co $2p$ core level of pure Co_3O_4 and ZC1, ZC5, and ZC25. The satellite peak is displaced in all the just mixed samples with respect to pure Co_3O_4 .

interesting to emphasize that the observed FM is not induced by metallic Co clusters since no metallic cobalt was detected by HRTEM or XPS. In the case of the ZnO particles, Zn $2p_{3/2}$ core level peak appears at 1021.7 eV suggesting that cobalt has not in diffuse into the ZnO lattice so Co is not doping the ZnO structure.

The superficial reduction of the Co_3O_4 nanoparticles was confirmed by Raman spectroscopy. A displacement of the bands is observed after mixing Co_3O_4 with ZnO when compare with pure Co_3O_4 , see Fig. 3. This displacement can be interpreted as a partial reduction of the Co_3O_4 nanoparticles to CoO. This displacement is more noticeable for the ZC1 sample, in which Co_3O_4 particles see more ZnO during the milling process. Then, it can be concluded that the role of ZnO is to promote this superficial reduction.

Based on the previous results, it could be reasonable to propose that the RT ferromagneticlike behavior is due to a core-shell model in which an antiferromagnetic nanoparticle (Co_3O_4) is inside and surrounded by a CoO-like shell at the surface. Thus, the anomalous magnetic properties must be related to an interaction between the shell spins (in which Co^{2+} is in octahedral coordination) and the core spins (in which Co^{2+} is in tetrahedral coordination). The finding supports that the origin of this FM is not related to the doping required for the DMS approach but to a superficial effect. This magnetism is different from the one that we previously

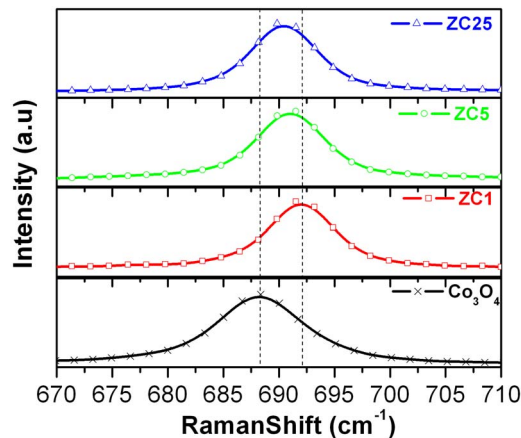


FIG. 3. (Color online) Comparison of Raman spectra comparison of pure Co_3O_4 with the different mixtures ZC1, ZC5, and ZC25 as milled.

reported for the ZnO/ MnO_2 system since there is no heat treatment or diffusion front or new phase formation.¹¹ However, it is a “new magnetism” ascribed to the particle surface.

In order to determine if this phenomenon is only due to the interaction of Co_3O_4 with ZnO or it is more general, the same preparation procedure was performed by mixing 1% Co_3O_4 with other oxides, with semiconducting and insulating properties, such as TiO_2 and Al_2O_3 (Fig. 4). The starting TiO_2 powder exhibits a room temperature magnetic behavior with an M_s of 1×10^{-4} emu/g TiO_2 , probably due to impurities of the starting powders. However, a strong increase of $>60\%$ was detected in the $\text{TiO}_2/\text{Co}_3\text{O}_4$ mixture. Moreover, RT magnetism is also found when Co_3O_4 is mixed with an insulator with pure diamagnetic signal, such as Al_2O_3 (Fig. 4). This stresses the relevance of this surface magnetism, which appears in mixtures with paramagnetic and diamagnetic behavior, but also with semiconducting and insulating properties. The role of these materials seems to be the reduction of the Co_3O_4 surface, although it cannot be ruled out that these materials also could align the uncompensated surface spins of Co_3O_4 though an interfacial induction since they are stucked close together.

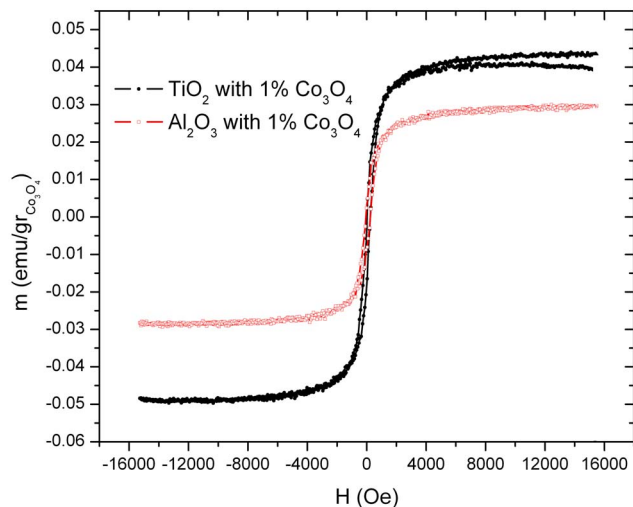


FIG. 4. (Color online) M vs H curves for different mixtures of 1 wt% Co_3O_4 with oxides such as TiO_2 and Al_2O_3 at RT (the paramagnetic contribution was subtracted).

In conclusion, it has been established that the presence of RT magnetic properties in the just mixed ZnO/Co₃O₄ samples is not related to a DMS behavior. It appears to be due to core-shell model in which an antiferromagnetic Co₃O₄ core (in which Co²⁺ is in tetrahedral coordination and Co³⁺ in octahedral coordination) is surrounded by a CoO-like shell (in which Co²⁺ is in tetrahedral coordination). Moreover, this magnetism is not only exclusively related to the interaction between Co₃O₄ and ZnO particles since it is observed with other oxides such TiO₂ and Al₂O₃, with semiconducting and insulating properties. Thus, we are dealing with an interesting magnetism related with the nanoscale and with the surface of the particles that leads to a RT ferromagneticlike behavior not previously reported.

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