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Ferromagnetism in bulk Co-Zn-O

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The origin of ferromagnetism in diluted magnetic semiconductors is still an open question, yielding a great deal of research across the world. This work focuses on the Co-Zn-O system. Room-temperature ferromagnetism is observed after a partial reaction of Co_3O_4 and ZnO, which can be ascribed neither to carrier mediation nor segregated cobalt metallic clusters. Another mechanism is yielding room-temperature ferromagnetism. This mechanism is associated with a partial reaction of ZnO and Co_3O_4 grains, and always appears when the starting phases (Co_3O_4 and ZnO) are present in the sample, suggesting that interfaces are involved in the origin of the observed ferromagnetism. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2399884]

I. INTRODUCTION

The search for diluted magnetic semiconductors (DMS) with Curie temperature above room temperature (RT) has recently attracted much attention. According to the theoretical predictions,[1,2] doping certain semiconductors with a few transition metal atoms would lead to RT ferromagnetism (FM). This FM is carrier mediated; thus, the conduction electrons would be spin-polarized, and DMS would then be excellent materials for next-generation spintronic devices.[3–6] In particular, considerable work has been carried out using ZnO as the semiconductor matrix, as it is a wide band gap, optically transparent semiconductor, and therefore useful in many optoelectronic applications. RT FM has already been reported in ZnO doped with Co,[7,8] and with other transition metals (Ni and Mn, for example).[9,10] However, the origin of ferromagnetism in these systems is still a matter of discussion. For instance, in the Mn-Zn-O system, Kundaliya *et al.*[11] suggest that the RT FM is due to a metastable secondary phase, but we attribute it to an interface double-exchange mechanism between Mn^{3+} and Mn^{4+}.[12]

For the Co-Zn-O system, the situation is still more complicated as segregation of small metallic Co clusters can lead to RT FM,[13–16] so the origin is not definitely established either. Some authors also claim that the FM observed is mediated by carriers in a spin-split impurity band derived from extended donor orbitals.[17] A third possible origin discussed in the literature is the weak FM of CoO.[18] CoO is well known to be antiferromagnetic, with a Néel temperature of 291 K. FM has also been observed in bulk Co-Zn-O samples prepared by different techniques. Metallic cobalt appeared to be the origin of FM in samples prepared by the combustion method[19] because of the reduction atmosphere of the process. However, Lawes *et al.*[20] prepared bulk samples confirming the substitution of the magnetic ions in the semiconductor matrix and found no magnetic ordering in this system down to 2 K. No FM has been reported in samples made by the hydrothermal technique or by standard solid-state reactions, this behavior being attributed to the absence of free carriers and the antiferromagnetic coupling of nearest-neighbor cobalt ions.[21,22] These two causes for the absence of FM are corroborated by theoretical works.[15,23]

These controversial results between research groups suggest that the FM strongly depends on the technical method used in sample preparation. Thus, in this article we will focus just on bulk samples prepared by the ceramic method, with the motivation in mind of understanding the origin of the magnetic properties in the Co-Zn-O system.

II. EXPERIMENT

ZnO-x(Co_3O_4) samples with $x=0.01$, 0.05, and 0.25 (named ZC1, ZC5, and ZC25, respectively) were fabricated following the low-temperature procedure of Sharma *et al.*[6,24] as follows: high-purity (>99.99% Aldrich) ZnO and Co_3O_4 raw powders were used for sample preparation. In a first step, powders were attrition milled in water medium with zirconia balls, dried, sieved, and prereacted afterward at 400 °C for 8 h separately in an alumina crucible. After that step, calcined powders were mixed and attrition milled again, and the dried and sieved powders pressed into disks 20 mm in diameter and 2 mm thick. The disks were then thermally treated between 500 and 1000 °C for 12 h. Co_3O_4 samples, as cast, milled, and annealed following the same procedure, were also prepared for comparison purposes. The error in the determination of the samples composition is ±0.5% of the total Co_3O_4 content for each sample (e.g., for the ZC1 sample the Co_3O_4 composition is $1\pm0.005\%$).

The structural analysis of the samples was carried out with a Siemens D5000 x-ray diffractometer (using a mono-

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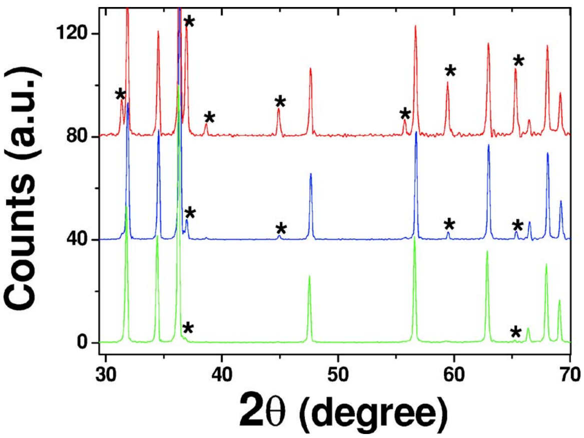

FIG. 1. (Color online) X-ray diffraction patterns for the ZC1, ZC5, and ZC25 samples after mixing by milling. Co_3O_4 diffraction maxima are indicated by asterisks; nonindexed maxima correspond to ZnO.

chromatic Cu $K\alpha$ line and operating at 40 kV and 40 mA). A vibrating sample magnetometer (VSM, JDL Instruments) was used for the magnetic characterization.

III. RESULTS

A. As-cast starting powders

The x-ray diffraction pattern from initial ZnO and Co_3O_4 powders (not shown) did not present any additional peak. Magnetic measurements of ZnO showed the well-known pure diamagnetic behavior, with a diamagnetic susceptibility at RT of -1.62×10^{-7} (emu/g×Oe). The magnetic characterization of the Co_3O_4 powder showed the expected paramagnetic (PM) behavior at 300 K [Co_3O_4 is antiferromagnetic, with a Néel temperature of $T_N \sim 33$ K (Ref. 25)] with $\chi(300\text{ K})=2.2\times10^{-5}$ (emu/g×Oe), plus the presence of a small ferromagnetic signal with a saturation magnetization of 1×10^{-3} emu/$g_{(Co_3O_4)}$. Co_3O_4 is usually obtained by oxidation of metallic cobalt in a water vapor atmosphere. Thus, some atoms in the metallic state may remain in the sesquioxide. Taking this into account, this small ferromagnetic component could be related to the presence of Co metallic clusters in the as-cast Co_3O_4. Actually, a 0.001% of cobalt atoms in the metallic state could account for this FM. The absence of peaks corresponding to metallic cobalt in the x-ray diffraction patterns would be justified by the fact that this percentage is well below the technique resolution. Results after the annealing processes explained below also confirmed this hypothesis.

B. Milled powders

The "so-called" ZC samples corresponding to the three compositions were studied after mixing the stoichiometric compositions by attrition milling in water medium but before any thermal treatment (not even prereacted at 400 °C). The structural x-ray diffraction analysis from the alloyed but not yet annealed ZC samples reveals no appearance of secondary phases. Only peaks from Co_3O_4 and ZnO are found in the x-ray diffraction patterns as shown in Fig. 1.

Obviously, the increase in the Co_3O_4 concentration for the three compositions yields an increase of the peaks from Co_3O_4 in the diffraction patterns. For instance, in the ZC1 sample, only the two more intense peaks are observed.

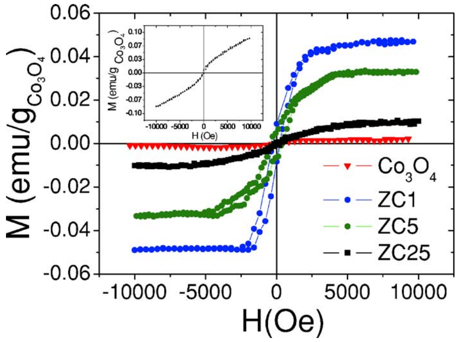

FIG. 2. (Color online) Magnetization curves at RT of the milled samples after subtracting the paramagnetic contribution. Inset shows the hysteresis loop for the ZC1 milled sample without the paramagnetic component subtraction.

Magnetization versus applied magnetic field curves were measured at 300 K (RT) for the three compositions. In the case of the ZC1 sample, a pure ferromagnetic behavior is observed in the curve. For the other two compositions and the Co_3O_4 sample, the ferromagnetic signal appears over a PM contribution. Hence, for the ZC1 sample the PM component is exactly compensated by the diamagnetic contribution of ZnO, while for the other samples with a larger content of Co_3O_4, the PM contribution overcomes the diamagnetism from ZnO. Figure 2 shows the magnetization curves of the three ZC samples after subtracting the PM contributions in order to display only the ferromagnetic component. Table I summarizes the values for the PM susceptibility and the ferromagnetic signal for these samples.

We observe that the ferromagnetic signal in the ZC samples after the mixing procedure is considerably higher than in initial Co_3O_4 (more than an order of magnitude). The highest saturation magnetization value corresponds to the ZC1 composition, and its value increases with the ZnO concentration of the samples.

In order to check if the variation of the magnetic properties during attrition milling was purely due to Co_3O_4, the initial Co_3O_4 powder alone was also milled; in this case the milling process did not modify the magnetic properties of the sample: the ferromagnetic component of this sample was exactly the same as for the as-cast Co_3O_4 [0.001 emu/g (Co_3O_4)], as Fig. 2 shows.

Although the x-ray diffraction (XRD) patterns reveal only the presence of the reactants in the sample, the increase of the FM signal after milling the samples containing ZnO indicates that some kind of interaction between ZnO and Co_3O_4 grains is taking place during the mixing process. Moreover, for milled samples, the larger FM signal corre-

TABLE I. Susceptibility of the paramagnetic component and saturation magnetization from the ferromagnetic one for the milled samples before any thermal treatment.

Sample	Co_3O_4	ZC1	ZC5	ZC25
χ χ_{PM} (emu/g×Oe)	2.2×10^{-5}	1×10^{-5}	1.3×10^{-5}	2.2×10^{-5}
M_S (300 K) (emu/g×Oe)	2×10^{-3}	5×10^{-2}	3.3×10^{-2}	3×10^{-2}

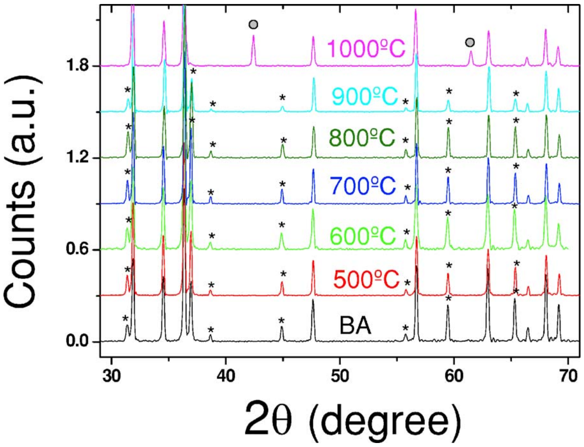

FIG. 3. (Color online) X-ray diffraction patterns from the ZC25 samples. Asterisks and circles indicate Co_3O_4 and CoO peaks, respectively. Nonindexed peaks correspond to ZnO. BA stands for before annealing.

sponds to the lower PM signal (see Table I), suggesting that some initial PM phase is transforming to FM during milling. The fact that the PM susceptibility is of the same order of magnitude for the three ZC samples in addition to the low values of M_S indicates that only a small fraction of the Co atoms is contributing to the ferromagnetic signal. As pure Co_3O_4 powder does not exhibit this modification of the magnetic properties after milling, such a modification involves an interaction of Co_3O_4 with ZnO. Actually, from Table I it is clear that the modification of the magnetic properties during milling is more evident for samples with a higher ZnO content, confirming that the interaction with ZnO is responsible for the modification of the magnetic properties of Co_3O_4.

Although 0.042% of Co atoms in the metallic state in sample ZC1 would give the FM signal observed, the increase of this signal cannot be attributed to segregation of metallic Co as no mechanism yielding the formation of more metallic cobalt can occur during the mixing process. However, a presumed DMS responsible for the FM observed cannot be discarded at this point, as this partial reaction could imply the substitution of a few Co atoms in the ZnO matrix.

C. Annealed samples

After annealing the three ZnO-containing samples at different temperatures in the 400–800 °C range, no changes are observed in the XRD pattern for any sample. However, as the $ZnCo_2O_4$ spinel is isostructural with Co_3O_4, we cannot determine from the patterns whether the spinel is forming or not.

Above 800 °C, for the samples ZC1 and ZC5 the maxima corresponding to Co_3O_4 disappear, but no new peaks appear. On the contrary, for sample ZC25, after annealing at 1000 °C, the Co_3O_4 disappears from the XRD pattern and the peaks corresponding to CoO arise (see Fig. 3). Hence, for all the samples, after annealing at 1000 °C there is no more Co_3O_4 present in the material up to the detection limit of our equipment. No evidence of metallic Co or any additional phase different than ZnO, Co_3O_4, and CoO was found for any sample up to the XRD resolution.

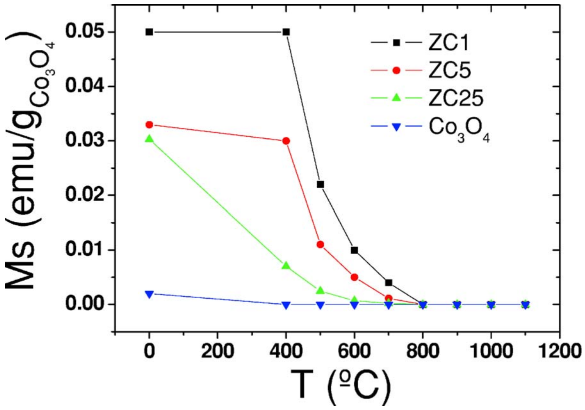

FIG. 4. (Color online) Saturation magnetization as a function of the annealing temperature.

The only reaction between Co_3O_4 and ZnO consistent with the XRD patterns is the formation of a solid solution $Zn_{1-x}Co_xO$ with a wurtzite-type structure, with the same lattice parameter as ZnO that would explain the fact that only peaks from the wurtzite structure of ZnO are observed in the diffraction patterns above the 800 °C treatment. In the ZC25 sample, the solubility limit of Co in ZnO is reached and an excess of Co_3O_4 remains in the sample after this reaction, which reduces to CoO (rock-salt crystal structure) at 1000 °C. This reduction is not observed for the other two compositions as evidence that all the Co_3O_4 present forms with ZnO the solid solution with a wurtzite-type structure mentioned earlier. The very small difference between the ionic radius of Co and Zn (75 and 74 pm, respectively) prevents us from seeing shifts in the maxima corresponding to ZnO wurtzite in the XRD diffraction patterns.

Annealing yields the decrease of FM for all the samples (see Fig. 4). For Co_3O_4, the FM vanishes after annealing at 400 °C (see Fig. 4), while it is still present for Zn-containing samples after annealing up to 800 °C. For Co_3O_4 it is clear that annealing in air promotes the oxidation of metallic Co clusters remaining in the sample, confirming the hypothesis that the ferromagnetic signal in this sample arises from those segregated clusters. The different behavior observed for the ZnO-containing samples suggests to us that the FM signal observed in these samples is not related to any metallic Co clusters, which should disappear after annealing at about 400 °C. The finite mobility of oxygen in these samples that would lead to an incomplete suppression of the magnetic moment of Co does not seem a reasonable cause for the FM observed. On one side, at 400 °C the reactants have barely interacted and the Co_3O_4 environment is generally identical to that of as-cast Co_3O_4. On the other, the FM vanishes at 800 °C for all the samples with ZnO, which is not consistent with the fact that the ZnO concentration in the sample is a key factor in the limitation of the oxygen mobility and different concentrations should lead to different vanishing temperatures of FM. Moreover, as no mechanism yields the appearance of more metallic Co in the samples during the mixing step, and after this milling the FM increases an order of magnitude its saturation magnetization value, we can thus reject the hypothesis of the segregated metallic cobalt clusters as the origin of FM in these samples.

It is worthy to note that for ZnO containing samples the FM signal is present up to 800 °C, the same temperature at which Co_3O_4 is still present in the sample according to the x-ray diffraction patterns. Thus, we can conclude that the wurtzite-type solid solution formed in this reaction is not responsible for the FM. Annealing at higher temperatures would yield a greater dispersion of the Co ions in the ZnO matrix if we suppose we are dealing with a DMS.[16] The decrease of FM with the subsequent anneals suggests that the origin of these magnetic properties is not associated with carrier-mediated mechanisms in a DMS.

Another possible origin invoked for the magnetic properties of this system is the weak FM of CoO.[18] We have also magnetically characterized CoO, and the sample presented a pure PM behavior at RT. Moreover, the fact that the appearance of CoO in the ZC25 sample after annealing at 1000 °C corresponds to a nonferromagnetic sample allows us to put aside the CoO hypothesis as a possible origin of the FM observed here.

The spinel $ZnCo_2O_4$ can never be invoked as the origin of the observed FM: as the treatment temperature increases, the amount of spinel present in the sample should also rise (as it promotes the Zn further diffusion), but the FM decreases, indicating that the spinel is not the origin of the ferromagnetic component of the samples either. Thus, the FM is associated with a partial reaction in which several phases (nonferromagnetic) are present in the sample. In this situation, the interfaces could play an important role in the observed ferromagnetic behavior (as found in the case of Mn-Zn-O).[12] If the FM signal arises from these interfaces, only a few atoms should contribute to the FM signal, explaining the low intensity of the FM signal. Moreover, after total reaction yielding a homogeneous composition, interfaces do not exist anymore, in agreement with the absence of FM in totally reacted samples.

We also notice that the largest saturation magnetization value corresponds to the ZC1 composition, indicating that the presence of ZnO enhances the ferromagnetic signal after alloying. This suggests that the partial reaction taking place between Co_3O_4 and ZnO during the mixing process, and associated with the FM observed, seems to be enhanced with ZnO concentration. This fact recalls the Mn-Zn-O system case, in which Zn diffuses into MnO_2 grains and where the increase in the Zn concentration favors this diffusion as the chemical gradient rises, the FM appearing at the interface of the diffusion front. A limited reaction of MnO_2 with ZnO also yields FM,[26] as happens in the samples studied in this work. In the case of Mn-Zn-O the double-exchange mechanism was invoked to account for the RT FM. However, double exchange is not well established for Co oxides, so this assignation is not straightforward in this case. Therefore, some so far unknown mechanism must be responsible for this FM, yet to be elucidated, and appearing after Co_3O_4 and ZnO partially react during the mixing step.

IV. CONCLUSIONS

In summary, we have shown that there is a mechanism promoting RT FM in Co_3O_4-ZnO bulk samples different than carrier mediation or segregated cobalt metallic clusters. After the mixing step by milling in water medium of the starting raw powders a partial reaction takes place, giving rise to a FM component. Annealing yields the decrease of FM that is only present when several phases are present in the material, pointing out interfaces as the origin of the observed FM. Further work needs to be done in order to achieve thorough understanding of this mechanism.

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