Magnetic properties of the TiO_2-Co_3O_4 system

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Abstract

We report here the observation of ferromagnetism (FM) at 300 K in mixtures of TiO_2 and Co_3O_4 powders despite the antiferromagnetic and diamagnetic character of both oxides respectively. The ferromagnetic behavior is found in the early stages of reaction and only for TiO_2 in anatase structure; no FM is found for identical samples prepared with rutile-TiO_2 . Optical spectroscopy and X-ray absorption spectra confirm a surface reduction of octahedral $Co^{+3} \rightarrow Co^{+2}$ in the mixtures which is in the origin of the observed magnetism.

Introduction

The appearance and control of magnetism in traditionally non-magnetic oxides is nowadays one of the most active and pursued goals of material physics [1]. In the last years, the research has been focused mainly on oxides doped with magnetic ions (the so-called Diluted Magnetic semiconductors). Recent results [2,3,4,5] indicate that the appearance of magnetism in these oxides (mainly ZnO, and TiO_2) is related to the presence of defects and surface/interface effects [6,7] but the origin of most of the experimental results is still unclear [8]. Actually, results are hardly reproducible and findings from different groups are commonly contradictory. Understanding this lack of reproducibility is probably one of the main challenges to determine the origin of this magnetism.

A common feature of all the experimental observations of magnetism is that signals are very weak, suggesting that only few atoms are involved in the magnetic response. Thus, it has been proposed that the emerging magnetism in oxides correspond to surface/interface magnetism [9,10,11].

It is really tough understanding the origin of this magnetism based only on magnetic measurements, since signals are very weak and effects from the rest of the material as impurities could mask the signals coming from interfaces. In this framework, correlating the magnetic properties with other measurements sensitive to the electronic structure can help to clarify this magnetism. This is the case for optical measurements, as the energy of photons involved in the processes allows discriminating between different processes arising at different atoms. Furthermore, optical properties are particularly sensitive to surfaces as the broken symmetry of the surface induces new electronic levels (surface states), so they can be especially useful for the investigation of surface effects.

In this work we study the magnetic properties of TiO_2 and Co_3O_4. Both oxides are mixed in powder form and thermal treated to promote their

interaction. Optical and X-ray absorption measurements are used to identify the origin of the observed room temperature magnetism. The difficulties to reproduce experiments in this kind of materials are also addressed.

Experimental

Samples were prepared by mixing powders of TiO_2 in anatase (A-TiO_2) and rutile structure (R-TiO_2) with 1% and 5% wt Co_3O_4. Analitycal grade powders were selected with average particles size in the submicronic range, typically 0.3-0.4 μm (see figure 1). Pure powders were magnetic tested in order to be sure that no ferromagnetic contributions were present. TiO_2 powder presented diamagnetic behavior and Co_3O_4 paramagnetic one. When subtracting the paramagnetic behavior, some Co_3O_4 samples exhibited a weak ferromagnetic like contribution with magnetization below $5 \cdot 10^{-4}$ emu/g that disappeared after annealing at 400°C [11]. This residual magnetization due to trace impurities was taking into account and adequately subtracted from the magnetic measurement of mixtures. Any powder with higher ferromagnetic-like behavior was considered as contaminated and completely discarded. Initially, the powders were mixed and milled in a attrition mill with zirconia balls for 15 minutes and subsequently they were thermally treated in air during 12 hours at different temperatures between 500°C and 900 °C. Selected raw materials were also processed following the same procedure to verify experimental conditions. Three different sets of samples were independently prepared at different laboratories (corresponding to authors´ affiliations 1, 2 and 3). Processing was managed by avoiding any kind of metallic tools to prevent contamination
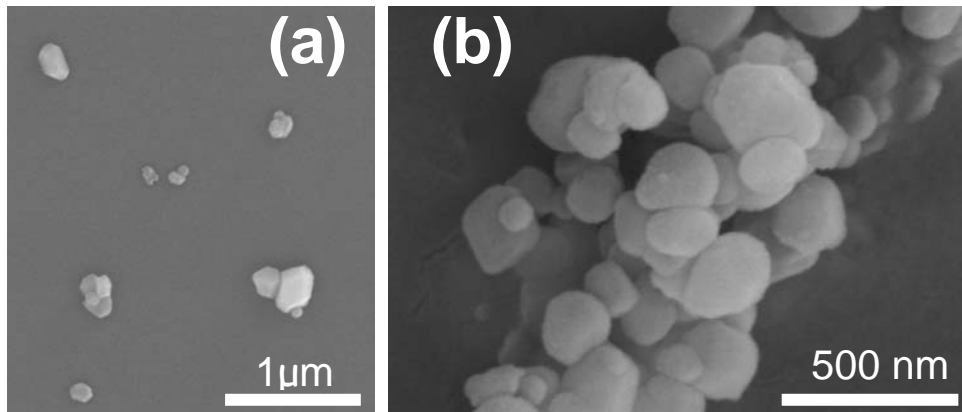
Figure 1. SEM images from (a) Initial Co_3O_4 powder. (b) 99%A-TiO_2-1%Co_3O_4 sample milled.

The structural analysis of the samples was carried out with a Siemens D5000 X-Ray Diffractometer using a monochromatic Cu K line and operating at 40 kV and 40 mA. Magnetic characterization was performed in three different Vibrating Sample Magnetometers: a VSM LDJ Instruments, a Quantum Design PPMS-VSM and a VSM Lakeshore 7304. . For the magnetic measurements, all possible sources of experimental errors described in [12] were taken into account. Optical absorption was measured with a Shimadzu 3101 spectrophotometer attached with an integrating sphere. X-ray Absorption Spectroscopy was performed at beamline BM25 (SpLine) in the European Synchrotron Radiation Facility at Grenoble.

Results and discussion

Figure 2 presents XRD measurements for the samples prepared using R-TiO_2. Up to annealing temperatures of 600°C only the initial R-TiO_2 (R) and Co_3O_4 phases are observed in the XRD patterns. After annealing at 700°C, for the samples with 5%Co_3O_4 some peaks from $CoTiO_3$ appear, coexisting with the initial phases. These data confirm that at this temperature the reaction between both phases has started. The peaks are scarcely identified for the samples with 1% Co_3O_4. This is quite reasonable since the amount of $CoTiO_3$ that can be formed is limited mainly by the concentration

of Co_3O_4 in the sample. Thus, the differences between both samples seem more related to the detection limit of the experimental setup than to structural differences. As the temperature increases over 700°C, the peaks from $CoTiO_3$ also does, while the Co_3O_4 ones decrease, disappearing at 800°C. At this temperature, all the Co_3O_4 in the sample has reacted with the TiO_2 to form the $CoTiO_3$. Due to the small fraction of Co_3O_4 there is an excess of TiO_2 that remains unaltered in the sample at all the annealing temperatures, as evidenced in the XRD patterns.
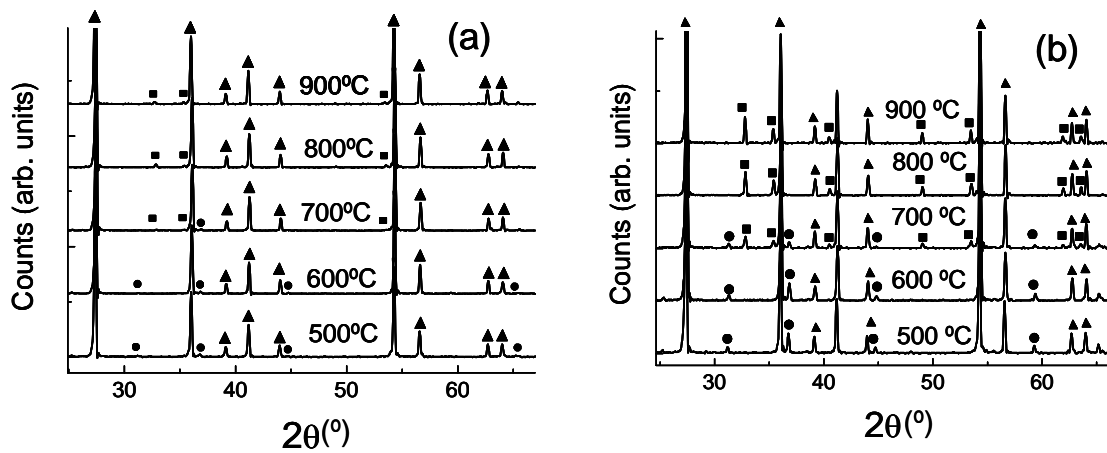

Figure 2. XRD patterns from R-TiO_2 with (a) 1% mol of Co_3O_4 and (a) 5% mol of Co_3O_4. Symbols stand for (▲) TiO_2 rutile, (●) Co_3O_4, (■) $CoTiO_3$.

Summarizing, the annealing process induces the interaction between both phases, consisting in the reaction of the Co_3O_4 with a small amount of R-TiO_2 to form $CoTiO_3$. The reaction starts below 700°C and is completed over 800°, when all the Co_3O_4 has reacted to form the spinel phase that coexists with the excess of R-TiO_2.

The XRD patterns from the samples prepared with A-TiO_2 results more complicated (figure 3). As in the case of R-TiO_2, up to 600°C only the initial phases are observed in the XRD diffractograms. After annealing at 700°C the presence of scarce peaks, ascribed to $CoTiO_3$ coexisting with the initial phases, indicates a partial reaction. Simultaneously, peaks from R-TiO_2 appear, confirming that the transformation of A-TiO_2→R-TiO_2 has started at this temperature. The presence of $CoTiO_3$ increases with the

temperature of the thermal treatment, while the transformation of A-$TiO_2 \rightarrow R\text{-}TiO_2$ is completed at 900°C. At this temperature, only R-TiO_2 and $CoTiO_3$ are present in the sample (as for the samples prepared with R-TiO_2).

Therefore, for these samples, the annealing produced two simultaneous processes: The reaction of TiO_2 with Co_3O_4 (similar to that produced in samples with R-TiO_2) and the transformation A-$TiO_2 \rightarrow R\text{-}TiO_2$.
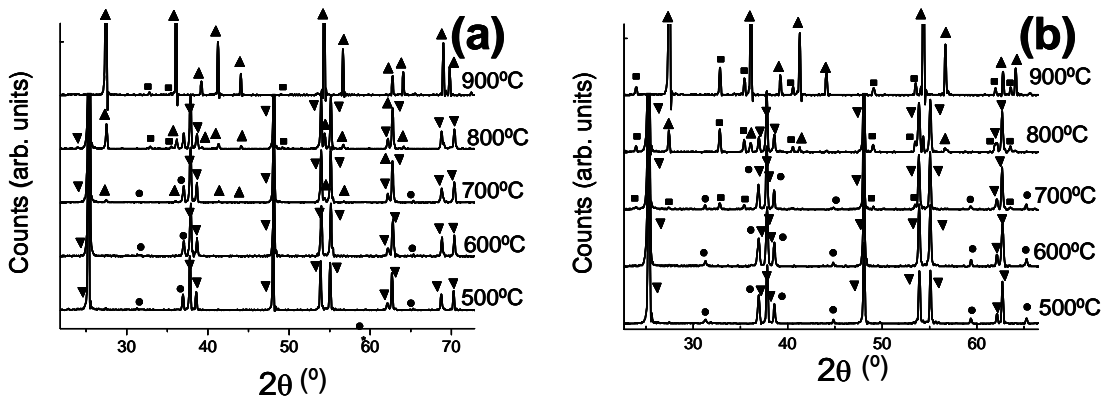

Figure 3. XRD patterns from A-TiO_2 with (a) 1% mol of Co3O4 and (a) 5% mol of Co_3O_4. Symbols stand for (▼) TiO_2 anatase, (▲) TiO_2 rutile, (•) Co_3O_4, (■) $CoTiO_3$.

Magnetic characterization of the samples is presented in figure 4. The overall behavior is paramagnetic with susceptibility decreasing up to annealing temperature of 500°C and increasing for higher temperatures. According to XRD diffractograms, the increase in magnetic susceptibility is due to the reaction of the Co_3O_4 with the TiO_2 to form $CoTiO_3$ that has a larger magnetic susceptibility than Co_3O_4 [13,14]. Differences in the value of magnetic susceptibility for rutile and anatase samples can be explained in terms of the different kinetic of the reaction with Co_3O_4. Rutile exhibits a closer structure than anatase [15], so the reaction with Co_3O_4 is slower than for anatase, that exhibits a more open structure and is therefore more reactive. Hence, for a fixed temperature, the degree of transformation is smaller for rutile, and the magnetic susceptibility

decreases accordingly (as the transformed $CoTiO_3$ exhibits larger susceptibility).
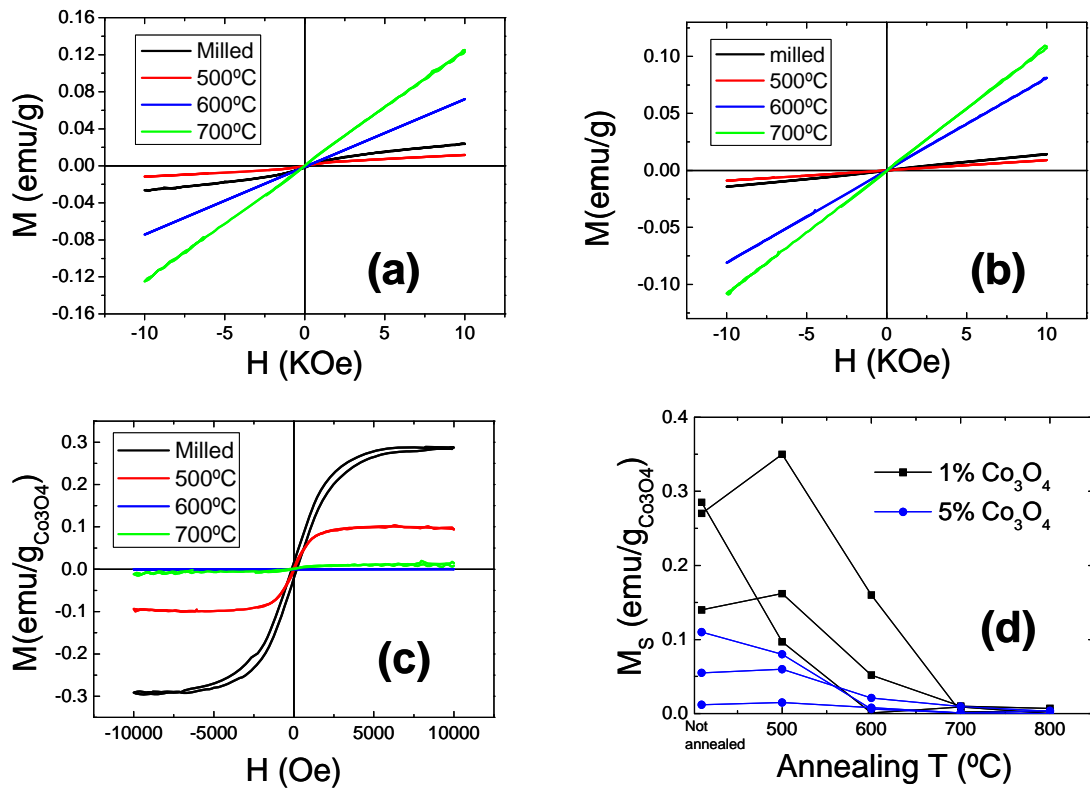

Figure 4. Magnetization curves for 99% TiO_2 - 1% Co_3O_4 samples for different annealing temperatures for (a) A-TiO_2 and (b) R-TiO_2. (c) Curves for the samples with TiO_2 in anatase structure after subtraction of a paramagnetic (linear) component.(d) Ms of the ferromagnetic component of the samples prepared with A-TiO_2 with 1% and 5% wt of Co_3O_4.

Despite the diamagnetic character of TiO_2, and antiferromagnetic behavior of Co_3O_4 and $CoTiO_3$ (with Neel temperatures of 42K and 37K respectively) we found a ferromagnetic contribution at room temperature for the samples with Co_3O_4 and A-TiO_2 milled and after annealing at low 500°C and 600°C (figure 4c); this contribution is absent for the R-TiO_2 samples in all the range of temperatures.

The experiment was repeated three different times at different laboratories, using oxides from different suppliers with similar specifications and different experimental setups. While the quantitative results are different (see figure 4d), in all three cases we found the same

effect: Ferromagnetism at room temperature appears only when using A-TiO_2 structure and after annealing at low temperatures (below 700°C). Quantitative differences appear in the maximum value of M_S, which ranges from $3.6 \cdot 10^{-1}$ to $1 \cdot 10^{-1}$ emu/g_{Co3O4}. The highest M_S in the presented data appears after milling, while for the other two sets it is found after 500°C annealing (figure 4d). For the samples with 5% of Co_3O_4, the effect also exists, although the value of M_S is fairly smaller than for those samples with 1%Co_3O_4. The paramagnetic component, on the other hand, is found to be basically the same for the samples annealed at the same temperature but prepared at different laboratories.

The appearance of room temperature magnetism in TiO_2 based materials containing cobalt only for the anatase structure is in agreement with most of the experimental results published for the Ti-O-Co system [16,17,18,19,20] while scarce experiments are found for R-TiO_2 [21].

However, the appearance of magnetism just after a short milling is surprising as no diffusion or strong interaction is expected at this stage. Such behavior indicates some interaction between TiO_2 and Co_3O_4 just after milling. The weak ferromagnetic signal suggests that only a small part of the material exhibits ferromagnetic behavior, which is consistent with the non ferromagnetic behavior of TiO_2 and Co_3O_4, the only phases observed by XRD in the ferromagnetic samples. The magnetic signal could then arise at the interfaces between both oxides, that are modified in the first stages of the reaction, and are not detected by XRD since they represents a very small fraction of the whole material.

In order to confirm that this early interaction leads to a modification of the electronic configuration of the oxides, we performed optical measurements. Optical absorption spectra for the samples with 5% of Co_3O_4 after the different thermal treatments are presented in figure 5.

Results for the samples containing 1% of Co_3O_4 were similar (although the features arising from the Co_3O_4 are not so clearly resolved).
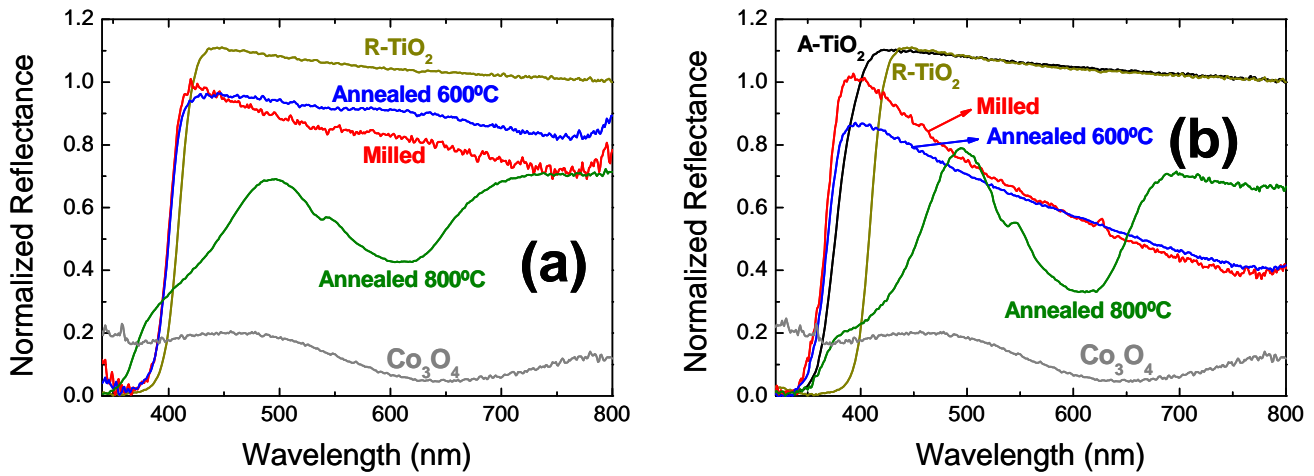

Figure 5. Normalized Reflectance for the samples containing 5% wt Co_3O_4 prepared with (a) rutile and (b) anatase TiO_2. Spectra from R-TiO_2, A-TiO_2 and Co_3O_4 are also presented for comparison pruposes.

Both A-TiO_2 and R-TiO_2 samples exhibit slight shifts in the edge after milling. This process acts as a very efficiency homogenizer procedure that favours the appearance of Co_3O_4-TiO_2 particle contacts during the drying step because of Van der Wall forces (figure 1). It is well known that the optical processes are very sensitive to surface effects, which introduce new electronic levels that may act as preferential recombination centres that can account for the observed shifts.

The samples exhibiting ferromagnetic behavior (those prepared with anatase and mixed and low temperature annealed) exhibit a maximum in the reflectance at the edge (390-400 nm) which is absent in all the other samples. This maximum the combination of the TiO_2 edge and a broad absorption band in the green-red par of the spectrum. Actually, the magnetic samples are the only ones exhibiting a blue coloration as the photos in the suplmentary info (figure S1) illustrates. It is particularly noteworthy that the equivalent samples prepared with R-TiO_2 show grey color.

Blue color is characteristic of compounds containing Co^{+2} atoms in octahedral positions [22]. However, Co_3O_4 presents the spinel structure with the Co^{+2} ions in thetraedral (T) positions and the Co^{+3} ions in octahedral (O) ones [14]. Thus, the blue color could be explained by a reduction of the Co^{+3} ions in O positions to Co^{+2} because of the interaction with the $A-TiO_2$. In order to check this hypothesis, we performed X-ray absorption spectroscopy in the Co K-edge.

Figure 6 presents the XAS spectra at the Co K-edge of pure Co_3O_4 and samples $95\%TiO_2-5\%Co_3O_4$ samples prepared with $A-TiO_2$ and $R-TiO_2$.
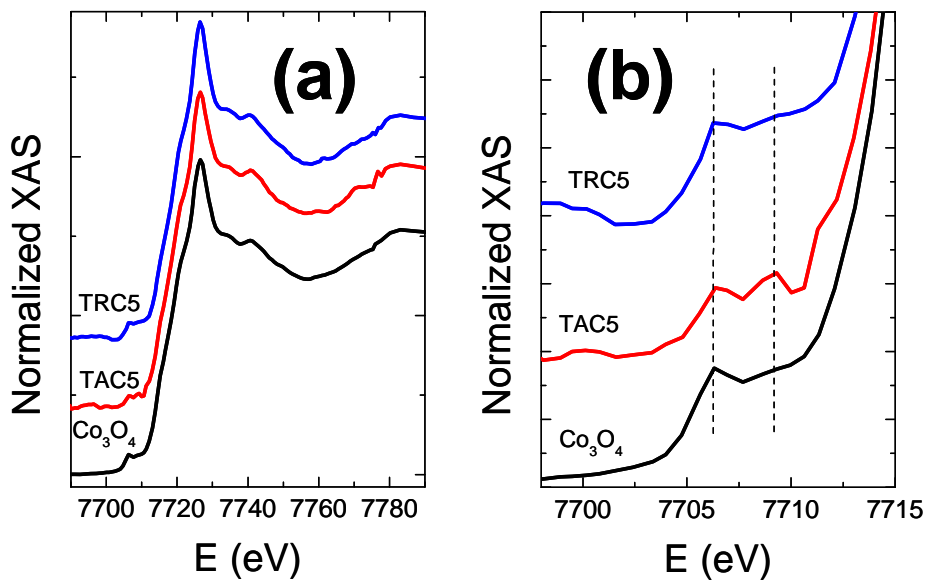

Figure 6. (a) XANES spectra at the Co K-edge for pure Co3O4 and samples 95%TiO2-5%Co3O4 samples prepared with $A-TiO_2$ (TAC5) and $R-TiO_2$ (TAC5) . (b) Detail of the pre-edge region.

The spectra (figure 6a) are very similar as expected since interaction between both oxides will be limited to a narrow surface region. No clear shift of the edge is found. However, the detail of the pre-peak shown in figure 6b evidences some changes. The feature in the Co_3O_4 spectra at about 7707 eV correspond to a bound 1s to 3d transition of tetrahedrally coordinated metal ions [23,24] which is forbidden for positions with a

center of inversion as octahedral positions. Therefore, for Co_3O_4, this peak is characteristic of Co^{+2} in tetrahedral positions. The pre-peak feature is very similar for the sample prepared with $R-TiO_2$ confirming the weak interaction between TiO_2 and Co_3O_4 after milling in this sample. On the contrary, for the sample with $A-TiO_2$, the peak is reduced and splits into two, corroborating the modification of the Co electronic structure. The appearance of a new peak at about 7709 eV has been ascribed to Co in tetrahedral position with a lower oxidation state [25], which agrees with results of the optical spectroscopy and confirms the surface $Co^{+3} \rightarrow Co^{+2}$ reduction in these sample. In our case, the vicinity of Ti atoms may break the octahedral symmetry inducing a distortion that can allow the presence of the pre-peak. Calculations (not presented here) of the XANES spectrum for a TiO_2/Co_3O_4 interface with Co^{+2} in octahedral positions, shown a double pre-peak at the same positions than those observed experimentally. A similar behavior was observed for the samples annealed at 500°C and 600°C that exhibit also ferromagnetic signals (see supplementary info figure S2).

These results confirms that the early interaction of the Co_3O_4 with the $A-TiO_2$ induces the reduction of the Co^{+3} in O positions to Co^{+2}, while this effect is not observed in the samples prepared with $R-TiO_2$. As concerns the origin of the interaction, a electrochemical solid state reaction taking place at the oxides surface has been proposed [26].

Optical and XAS spectroscopy studies, points on the Co reduction as the origin of the ferromagnetic signal. As indicated above, Co_3O_4 present the spinel structure as most of the ferrimagnetic materials, like Fe_3O_4 or $NiCo_2O_4$, with the Co^{+2} ions in T positions and the Co^{+3} ions in O ones [14]. For this structure, the predominant interaction is the antiferromagnetic super-exchange between T and O positions, while interaction T-T and O-O are also antiferromagnetic but much weaker than the T-O one. Consequently, there are two magnetic sublattices corresponding to T and O position with antiparallel orientation. Therefore these spinels exhibit

ferrimagnetic behavior with high order temperature (T_C=858 K for Fe_3O_4, or 673 K for $NiCo_2O_4$). However, for Co_3O_4, Co^{+3} ions in O positions presents no magnetic moment due to the large splitting of the of the 3d orbital in this symmetry [14]. Hence, in Co_3O_4 only Co^{+2} in T position hold a magnetic moment and the T-T weak antiferromagnetic interaction is the dominant, so the system present antiferromagnetic behavior with a much lower order temperature of T_N=42 K. However, for Co^{+2} atoms in a octahedral field, the orbital splitting is quite small and Co^{+2} atom in this symmetry should hold a magnetic moment [14]. For a region of the crystal were Co^{+3} in O positions are reduced to Co^{+2} there will be magnetic moments in both O and T position with t_{2g} orbitals partially filled. In this situation, T-O antiferromagnetic interaction would be the dominant one and the system should present a behavior similar to that of Fe_3O_4, that is, ferrimagnetism with high order temperature (due to the strong interaction T-O). Therefore, observed weak ferrimagnetic signal can be explained by the reduction of Co^{+3} in O positions to Co^{+2} demonstrated by XANES and optical spectra, and no new magnetic ordering mechanisms are required to account for it. However, the effect in Co_3O_4 will be restricted to very small surface regions; the spinel structure of Co_3O_4 is unstable if a large fraction of Co^{+3} is reduced to Co^{+2} promoting the transformation to CoO which is antiferromagnetic. Thus, it is not possible to obtain a bulk ferrimagnetic material nor a material whit uniform magnetic properties based on this effect.

Surface is the most sensitive part of the materials to any kind of treatment or interaction. Thus, nominally identical oxides from different suppliers can present identical bulk properties but fairly different surfaces. Properties depending on the surface and its reactivity in the first stages can be completely different, as we found for the three sets of samples analyzed here. This experimental fact could account for the discrepancies in results from different groups that use powder nominally

identical with the same bulk structure but different surfaces due to different origin. This idea is also supported by recent results [27] that show that a pre-calcination (just at 400°C) of ZnO alters its surface electronic structure and consequently its reactivity.

Conclusions

In summary, we demonstrated that a weak interaction between Anatase-TiO_2 and Co_3O_4 surface induces a surface reduction of Co^{+3} atoms in octahedral positions to Co^{+2} generating a weak ferromagnetic signal at room temperature. These magnetic signals can be explained as due to super-exchange interactions (as the situation is similar to that in Fe_3O_4) and no new magnetic ordering mechanisms are required to account for them. This demonstrates the possibility to observe weak ferromagnetic signals in samples containing Ti, O and Co that must be considered when studying the magnetic properties of $Co:TiO_2$ diluted magnetic semiconductors and similar materials.

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