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Reversible switching of room temperature ferromagnetism in CeO₂-Co nanoparticles

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We investigated the reversible ferromagnetic (FM) behavior of pure and Co doped CeO₂ nanopowders. The as-sintered samples displayed an increasing paramagnetic contribution upon Co doping. Room temperature FM is obtained simply by performing thermal treatments in vacuum at temperatures as low as 500 °C and it can be switched off by performing thermal treatments in oxidizing conditions. The FM contribution is enhanced as we increase the time of the thermal treatment in vacuum. Those systematic experiments establish a direct relation between ferromagnetism and oxygen vacancies and open a path for developing materials with tailored properties. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4705045>]

Diluted magnetic oxides¹ (DMOs) have been the focus of extensive research in the last years, due to the growing interest in finding materials for the emerging technology of spintronics.² The intriguing occurrence of room temperature ferromagnetism (RT-FM) in typically non-magnetic oxides under certain conditions have also attracted much attention in the field of condensed matter physics and there is major consensus that point defects like oxygen vacancies play a fundamental role in the emergence of this phenomenon.^{1,3,4}

Among the various oxides displaying this particular behavior is CeO₂, which in bulk is a diamagnetic insulator with proven capability as an oxygen ion conductor when doped with trivalent Sm or Gd ions.⁵ CeO₂-based systems have been thoroughly studied after the discovery of RT-FM on both pure^{6–10} and slightly doped^{11–14} samples. A large amount of effort has been devoted to the study of thin films^{3,12,13,15–19} (see also Ref. 1), while few works have focused on powdered samples.^{8–11,14} The use of powders is advantageous because the typically low magnetic signals of these systems can easily be enhanced just by increasing the quantity of the sample. In addition, the surface to volume ratio of the sample can be adjusted simply by performing adequate thermal treatments and this is particularly convenient as the surface is usually the preferred location of point defects.

In several works devoted to RT-FM in CeO₂, the high mobility of oxygen, and the consequent facility to create oxygen vacancies, is suggested as the cause for this peculiar behavior as this process would promote the presence of magnetic Ce³⁺ ions.^{3,15} However, it is still not clear whether a small amount of magnetic ions can give rise to long range interactions even in slightly doped samples. In any case, this point has not yet been established beyond doubt⁸ and even the presence of impurities²⁰ or clustering of the dopant²¹ has not been completely discarded as one possible answer

for the utterly unexpected magnetic behavior reported in the literature.

As magnetic signals in DMOs are typically small, extreme care must be taken during the synthesis procedure and handling of the samples to avoid contamination, and it is also important to carry out methodological studies to discard the possible influence of spurious magnetic impurities. In this work we performed a systematic study of the magnetic properties of CeO₂ nanopowders with particular focus on the influence of oxygen vacancies in both pure and doped samples. We show that an annealing process in vacuum can induce RT-FM in doped samples and paramagnetic (PM) behavior in pure samples. In all cases, this magnetic behavior can be erased by re-oxidation, ruling out segregation as responsible for the magnetic signal. The use of nanostructures allows us to enhance the surface to volume ratio, thus increasing the relative concentration of defects compared to bulk samples.

Pure and Co-doped CeO₂ powders were synthesized by the liquid-mix method using 99.99% Ce(NO₃)₆·6H₂O and cobalt(II) nitrate hexahydrate as reagents. All samples were calcined in air at 300 °C. Additional thermal treatments were performed at 500 °C, both in air at atmospheric pressure and in vacuum, using a mechanical pump to reach a pressure of around 4.10⁻² mbar, with dwell times between 4 and 30 h. Samples were labeled with a two-number code denoting the atomic percentage of Co (*x*), and the dwell time of the vacuum treatment (*dwt*) in hours, namely *x-dwt*. Magnetic measurements were performed in a VersalabTM VSM from Quantum Design. X-ray diffraction data was obtained at the ID27 beamline of the European Synchrotron Radiation Facility.

The X-ray diffraction analysis of our samples, indicate a fluorite structure with no secondary phases.²² The crystallite sizes of our samples are around 7 nm, obtained by the Scherrer equation. In samples doped with more than 15% of Co, we observed some impurity peaks which can be indexed with cubic Co₃O₄ but they never overpass 1% in weight fraction.

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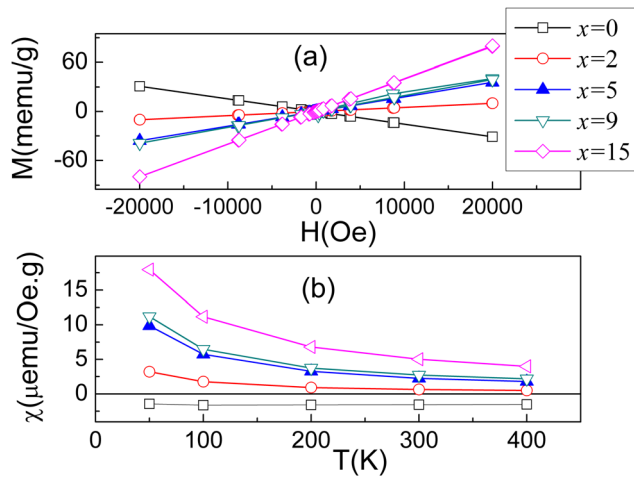


FIG. 1. (a) M vs H dependence for the as sintered samples at room temperature for different cobalt concentrations. (b) Magnetic susceptibility as a function of temperature.

In Figure 1(a) we show the magnetic measurements at 400 K for the samples synthesized in air for different doping concentrations. The behavior of the samples ranges from diamagnetic for the pure CeO_2 to an increasing PM signal upon doping. The magnetic component corresponding to the sample holder was previously measured and subtracted from all the presented data. Figure 1(b) shows the magnetic susceptibility of the as-sintered samples as a function of temperature. We see that the magnetic susceptibility of the pure sample is negative and almost temperature independent while the one corresponding to the doped samples displays the increasing PM tendency upon doping.

As we are interested in the role played by oxygen vacancies, we performed a series of thermal treatments in vacuum in order to de-oxygenate the samples. The color of the as-sintered samples change from yellow in the un-doped samples, to green in the doped ones. A first look at the samples treated in vacuum evidenced a darkening that strengthens when increasing the treatment time, possibly indicating changes in the optical band-gap and in turn, the electronic structure of the system.

Figures 2(a) and 2(b) show the M vs H dependence at 400 K of samples with $dwt = 4$ h. The system displays a significant change which evidences the crucial role played by oxygen vacancies. Magnetization measurements of de-oxygenated samples show a progressive evolution from a PM behavior for the low doped samples, to a FM response for samples with more than 9% of Co content. In fact, the magnetization of the doped samples is the result of the superposition of two components: a PM one and a FM one.

In Figure 2(c), we show measurements for samples with 9% of Co, with incremental dwt . In the samples treated in vacuum, the FM contribution is enhanced when dwt is increased. This result confirms the direct relation between the appearance of oxygen vacancies and the emergence of ferromagnetism. In the following, we present a separate analysis of the PM and the FM contributions to the magnetization.

The PM contribution to the magnetic susceptibility follows a Curie-Weiss law according to²³ $\chi = Np/[3k_B(T - \theta)]$, with N the number density, p the effective number of Bohr magnetons, and θ the Curie-Weiss constant. In all cases, a

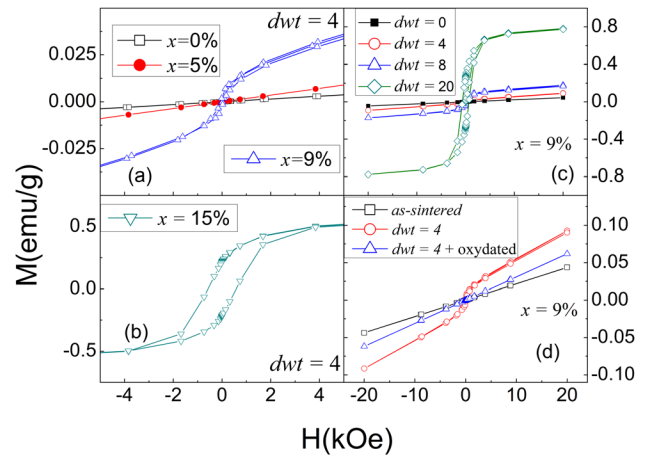


FIG. 2. (a) and (b) M vs H dependence at 400 K for samples treated in vacuum for 4 h. (c) M vs H dependence at 400 K for the samples with 9% of Co for different thermal treatments in vacuum. (d) M vs. H data for the sample with 9% of Co, measured for the as-sintered sample, the sample treated for 4 h in vacuum and the sample re-oxidated (in air at atmospheric pressure) after been treated in vacuum for 4 h.

negative θ was obtained of around -20 K. Non-reduced samples present $p \sim 3$, which suggests a magnetic contribution originated mainly by Co^{2+} ions. In fact, the cobalt reagent and the low temperatures used during the synthesis procedure, is consistent with this picture. In the samples treated in vacuum for 4 h, p increases to about 4, indicating either a Co^{3+} prominence or the presence of Co^{2+} with a larger quantity (compared with non reduced samples) of Ce^{3+} ions. Although we cannot rule out any of them, a strong suggestion in favor of the latter is that CeO_2 systems are very good oxygen ion conductors in presence of oxygen vacancies, a fact related to the facility of Ce ions to change from of Ce^{4+} to Ce^{3+} . In addition, recent calculations²⁴ showed that oxygen vacancies tend to group near cobalt ions favoring the presence of Co^{2+} and Ce^{3+} ions. No significant changes are observed for longer vacuum treatments.²²

In the samples with $x = 15\%$, we observed the presence of Co_3O_4 impurities. Co_3O_4 is PM as measured in our synthesized bulk samples and it is no possible to magnetically individualize this contribution and separate it from that of Co as dopant. However, as we observed only 1% of this impurity, the correction to the overall susceptibility should be minor. For smaller Co concentrations, the correction becomes insignificant.²² In addition, it is important to notice that the magnetic susceptibility of the pure sample with $dwt = 4$ h, is one order of magnitude below the one corresponding to doped samples. Thus the change from $p \sim 3$ to $p \sim 4$ is consistent with the appearance of some Ce^{3+} ions during the vacuum treatment.

In Figure 3, we present M_{sat} (namely, the saturation of the FM component of the magnetization) as a function of doping for the samples treated in vacuum for 4 h and as a function of dwt for samples with 9% of Co (Figures 3(a) and 3(b), respectively). The nonlinear growth of M_{sat} versus doping is consistent with an enhancement of the FM interaction, possibly related to the reduction of the distance between Co ions. In addition, the observed increment of M_{sat} versus dwt indicates that an increase in the concentration of oxygen vacancies is essential to explain the appearance of ferromagnetism. This

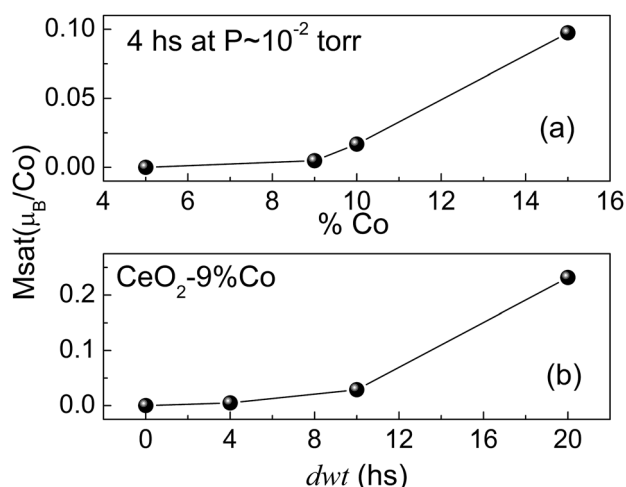


FIG. 3. (a) Saturation of the FM part of the magnetization (Msat) vs. (a) doping for samples treated in vacuum for 4 h and (b) dwell time of the treatment in vacuum (dwt).

result is in agreement with previous theoretical and experimental works^{11,14,17,23} suggesting that oxygen vacancies enhance FM behavior in the CeO₂-Co system.

Taking into account that the change in the magnetic properties only appears after thermal treatments, a doubt could be raised on the accidental incorporation of spurious magnetic impurities. In order to rule out this possibility, we have oxidated sample 9-4 by performing an additional thermal treatment at 500°C in air for 4 h. As shown in Figure 2(d), the induced FM behavior is reversible, which unambiguously establishes the relation of ferromagnetism with the presence of oxygen vacancies. In addition, the colors of the samples return to the original yellow (or green) for the pure (or doped) samples. No evidence was observed on our x-ray data regarding the presence of metallic cobalt; however, as a very small amount of it could give rise to a significant signal this is a fact that deserves further study.

We have also tried to induce ferromagnetism on the pure sample by performing thermal treatments in vacuum. We found that an extensive thermal treatment with $dwt = 30$ h can only induce a PM dependence. We observed only a small relative change of the magnetic signal when increasing the dwell time of the treatment from 10 to 30 h which evidences the futility of further increasing dwt and strongly suggests that we have reached an equilibrium state beyond which no changes are observed.²² Detailed investigation on the effect of pressure of the vacuum treatment and alternative de-oxygenation procedures are currently in progress.

In summary, we performed a systematic investigation of the magnetic properties of Co-doped CeO₂ nanopowders. We observed that the as-sintered samples display a PM behavior (diamagnetic for non doped samples) and RT-FM was obtained by performing thermal treatments in vacuum. RT-FM is enhanced as doping is increased and it can be erased by performing thermal treatments in air showing a reversible behavior. These facts strongly suggest that oxygen vacancies are one of the main reasons for the appearance of RT-FM in the CeO₂-Co system. In all cases, an intrinsic PM

component was observed superimposed to the FM one, indicating the heterogeneous nature of the nanoparticles, which is probably related to the fact that we are dealing with samples in which the surface to volume ratio is important. In fact, the effect of the size of the nanoparticles deserves a further study in its own right. The present study regarding the reversible switching of RT-FM offers a feasible opportunity to tailor the magnetic properties of oxides and paves the way for future investigations to develop materials.

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