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# Room-temperature ferromagnetism in pure and Co doped CeO<sub>2</sub> powders

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## Abstract

We report the room-temperature (RT) ferromagnetism (FM) observed in pure and Co doped CeO<sub>2</sub> powder. An insulating nonmagnetic CeO<sub>2</sub> single crystal, after grinding into fine powder, shows an RT-FM with a small magnetization of 0.0045 emu g<sup>-1</sup>. However, the CeO<sub>2</sub> powder became paramagnetic after oxygen annealing, which strongly suggests an oxygen vacancy mediated FM ordering. Furthermore, by doping Co into CeO<sub>2</sub> powder the FM can significantly enhance through a F-centre exchange (FCE) coupling mechanism, in which both oxygen vacancies and magnetic ions are involved. As the Co content increases, the FM of Co doped CeO<sub>2</sub> initially increases to a maximum 0.47 emu g<sup>-1</sup>, and then degrades very quickly. The complex correlation between the Co content and saturation magnetization was well interpreted by supposing the coexistence of three subsets of Co ions in CeO<sub>2</sub>. Our results reveal that the large RT-FM observed in Co doped CeO<sub>2</sub> powder originates from a combination effect of oxygen vacancies and transition metal doping.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

There is an ongoing quest for ferromagnetic semiconductors with a Curie temperature well above room temperature, which could be used for a second generation of spin electronics. Recently, several research groups have observed room-temperature ferromagnetism (RT-FM) in transition metal (TM) doped semiconductor oxides such as ZnO, TiO<sub>2</sub>, and SnO<sub>2</sub> films [1–4]. It is strange that high temperature ferromagnetic ordering is usually observed in TM doped films prepared under high vacuum conditions [1–5], but can rarely be found in TM doped single-crystal or polycrystalline bulk samples [6–10]. This phenomenon engendered an assumption

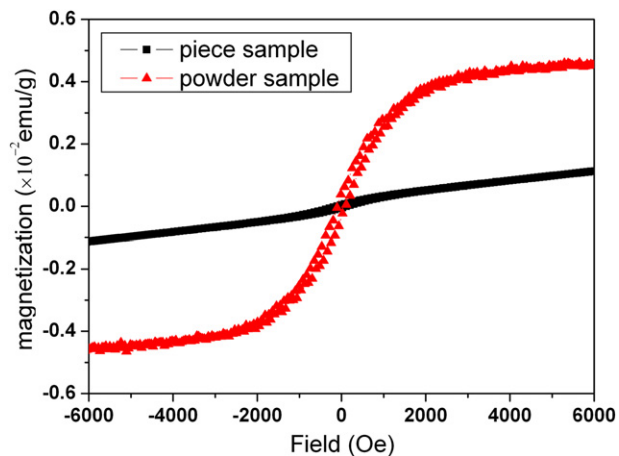
that the defects or oxygen vacancies induced by the vacuum deposition process are one of the most important origins of RT-FM. The assumption was strongly supported by the fact that having more oxygen could degrade the magnetic ordering [11–14], while increase of oxygen vacancies could enhance the FM [15]. Importantly, Coey's group reported magnetism observed in insulating HfO<sub>2</sub> thin films on sapphire or silicon substrates [16]. Tiwari *et al* also reported a giant magnetic moment of 8.2  $\mu_B/\text{Co}$  with a high Curie temperature of 875 K in Co doped CeO<sub>2</sub> dielectric films [17]. Even more surprisingly, RT-FM was also detected in undoped semiconducting and insulating oxide thin film such as SnO<sub>2</sub>, TiO<sub>2</sub>, and HfO<sub>2</sub> [18]. All these surprising results refer to the defect or oxygen vacancy mechanism. Under this circumstance, the spin-split impurity-band model [19], in which free carrier and TM doping is involved, for the RT-FM origin in diluted magnetic oxides is challenged. It is also doubtful whether the TM doping indeed plays a very important role in introducing RT-FM in those supposedly nonmagnetic oxide hosts. In the present work, we report some interesting results obtained in undoped and Co-doped bulk CeO<sub>2</sub> materials, attempting to clarify the role of defect or oxygen vacancies and TM doping.

## 2. Experiment

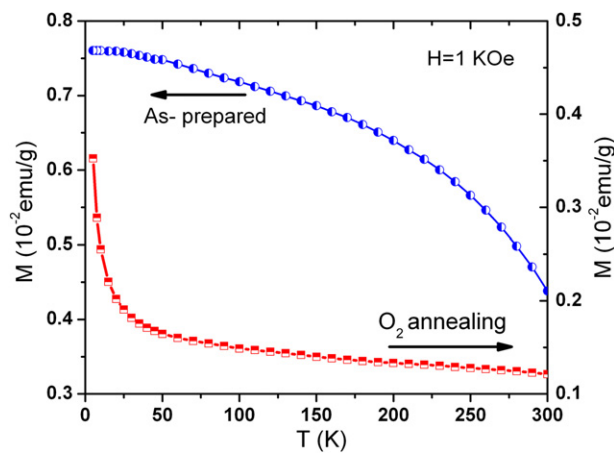
Pure single-crystal samples were prepared by cutting CeO<sub>2</sub> pieces from a pure single-crystal ceria. A part of a CeO<sub>2</sub> piece was ground into fine powder with particle size of 1–3  $\mu\text{m}$ . Ce<sub>1-x</sub>Co<sub>x</sub>O<sub>2- $\delta$</sub>  polycrystalline samples were fabricated by the standard solid-state reaction method with various contents of Co dopant. High purity CeO<sub>2</sub> (99.99%) and CoO (99.99%) powders were mixed thoroughly, pressed into pellets and sintered at 1400 °C for 10 h in air, and then carefully ground into fine powder for property measurements. The grinding process was carried out very carefully using a clean agate mortar and pestle to avoid any magnetic impurity contamination. The element valence analysis was carried out using x-ray photoelectron spectroscopy (XPS) and the elemental composition was determined with energy dispersive spectroscopy (EDS). The XPS was recorded on an XSAM800 spectrometer in XAT mode with a minimal resolution of 0.8 eV. Unmonochromated Mg K $\alpha$  x rays ( $h\nu = 1253.4$  eV) were used as the source with a high current (12 mA). The base pressure of the chamber is  $2 \times 10^{-7}$  Pa. The crystalline structure was characterized by x-ray diffraction (XRD, Bede TM 2000) with Cu K $\alpha$  radiation. The RT and low-temperature magnetic properties were measured using an alternating gradient magnetometer (AGM, Micromag TM 2900) with a resolution of  $1 \times 10^{-8}$  emu and a commercial superconducting quantum interference device (SQUID), respectively.

## 3. Results and discussion

Figure 1 shows the magnetization ( $M$ ) versus field ( $H$ ) curve of a pure single-crystal piece and powder. It is found that the crystal piece does not show a ferromagnetism signal, which is consistent with the results observed in pure TiO<sub>2</sub>, HfO<sub>2</sub> and In<sub>2</sub>O<sub>3</sub> bulk materials [18]. However, the fine powder sample exhibits a very well defined hysteresis loop, though the FM is weak, with a saturation magnetization of about 0.0045 emu g<sup>-1</sup>. Since the piece and the powder were prepared from an identical single crystal, the difference of magnetic behaviour cannot be attributed to substitutional impurities. As we know, ceria is a potential catalyst which easily forms oxygen vacancies at its surface. Also, several early studies show that CeO<sub>2</sub> is quite prone to form oxygen vacancies without changing its fluorite crystal structure [20–22]. It can thus be expected that a fairly large number of oxygen vacancies were generated during the grinding



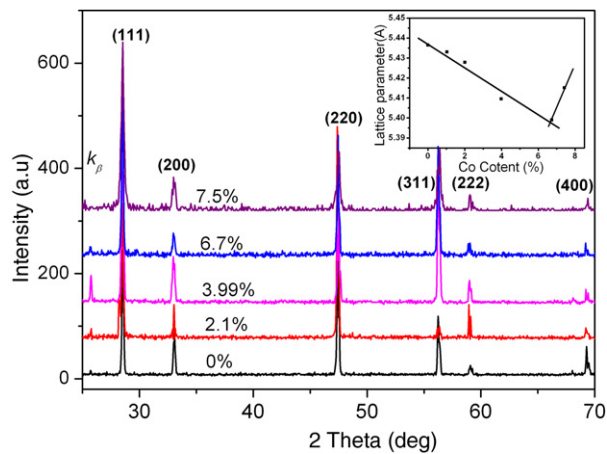
**Figure 1.** Magnetization ( $M$ ) versus magnetic field ( $H$ ) at 300 K for pure  $\text{CeO}_2$  piece and powder.



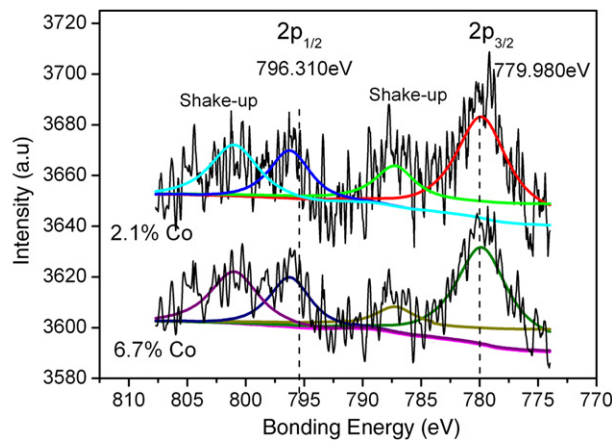
**Figure 2.** Magnetization versus temperature at 1 KOe for as-prepared and 2 h oxygen-annealed pure  $\text{CeO}_2$  powder.

process. These defect centres congregate mostly near the fringe of the powder, thus allowing a ferromagnetic coupling, and consequently give rise to the observed FM.

In order to clarify if the FM in pure  $\text{CeO}_2$  powder is really derived from the oxygen vacancy mechanism, the as-ground powder was annealed at  $500^\circ\text{C}$  for 2 h in an oxygen atmosphere with the pressure of 700 Torr. The magnetism versus temperature ( $M-T$ ) curves for the as-prepared and annealed samples were measured by SQUID. If oxygen vacancies are a real source of magnetism, then we must observe a clear difference in magnetic properties of the powder after oxygen annealing. From figure 2, one can see that the powder became paramagnetic after oxygen annealing process. So we can conclude that filling up oxygen vacancies destroys the ferromagnetic ordering in the powder. A first-principle calculation, using the full potential linearized augmented plane wave method and generalized gradient approximation within the density functional theory framework, was carried out to study the influence of oxygen vacancies on the magnetic properties of  $\text{CeO}_2$ . The calculation indicates that oxygen vacancies can pull the d and f orbits of Ce closer to the Fermi level, leading to a small exchange splitting [23].



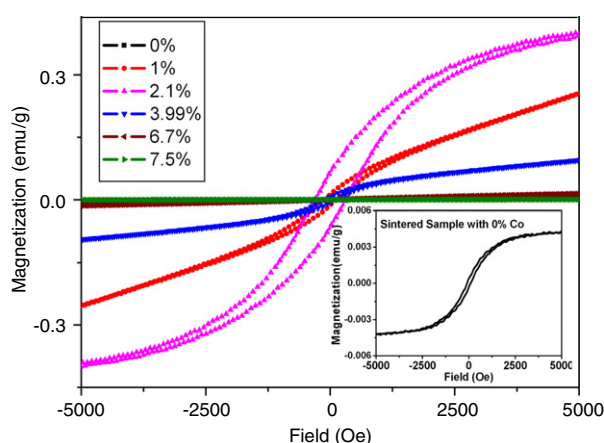
**Figure 3.** XRD patterns for CeO<sub>2</sub> powders with various Co concentrations. Inset: dependence of lattice parameter on doped Co content.



**Figure 4.** X-ray photoelectron spectroscopy (XPS) studies of Co 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks for the 2.1% and 6.7% Co doped CeO<sub>2</sub> powder.

These experimental and theoretical results strongly support that the oxygen vacancy does induce ferromagnetism into CeO<sub>2</sub> powder even with no TM doping.

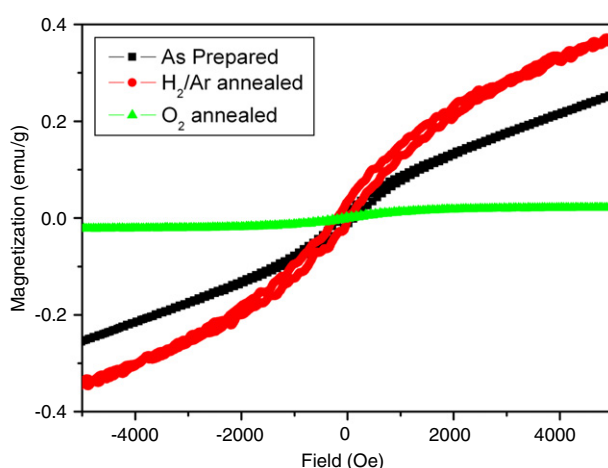
The XRD patterns of sintered Ce<sub>1-x</sub>Co<sub>x</sub>O<sub>2-δ</sub> powder were collected and are shown in figure 3. The Co content was determined by EDS to be  $x = 0, 0.01, 0.021, 0.0399, 0.067,$  and  $0.075$ . One can see from figure 3 that the patterns exclusively show diffraction peaks corresponding to CeO<sub>2</sub> fluorite structure even with Co content as high as 7.5%. None of the samples in this compositional range showed any evidence of impurity phases. As the amount of Co increases from  $x = 0$  to 0.04, the x-ray peak widths decrease, suggesting that crystalline quality is improved. Evolution of lattice parameters, as obtained from the Rietveld refinement, with  $x$  is shown for Ce<sub>1-x</sub>Co<sub>x</sub>O<sub>2-δ</sub> in the inset of figure 3. The lattice constant ' $a$ ' or ' $c$ ' decreases with  $x$  from 0 to 0.067. This behaviour is expected according to the substitution of the bigger Ce<sup>4+</sup> ion (radius = 0.97 Å) by the smaller Co<sup>2+</sup> ion (radius = 0.72 Å). At  $x = 0.075$ , the lattice constant slightly increases, implying a possible solubility limit for cobalt in CeO<sub>2</sub>. The XPS spectrum of samples with 2.1% and 6.7% Co is shown in figure 4. The



**Figure 5.** Magnetization versus magnetic field curves for the Co doped  $\text{CeO}_2$  at room temperature. Inset is the enlarged  $M-H$  curve of undoped  $\text{CeO}_2$ .

peaks for  $\text{Co } 2p_{3/2}$  and  $2p_{1/2}$  and their shake-ups were fitted using the Gaussian method and the resulting  $\text{Co } 2p_{3/2}$  and  $2p_{1/2}$  core levels for  $\text{Co-O}$  bonding were found to be at 779.98 eV and 796.31 eV, respectively. This XPS feature, according to Zhang [2], excludes the possibility of the Co cluster formation. Tiwari *et al* have mentioned that the Co ion in  $\text{Ce}_{1-x}\text{Co}_x\text{O}_{2-\delta}$  is in a mixed oxidation state with  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  coexisting together [17]. We further confirmed this observation by comparing the XPS spectrum of samples with different Co. As the  $2p_{3/2}$  binding energies of  $\text{Co}^{2+}$  are relatively close to that of  $\text{Co}^{3+}$ , the two oxidation states of cobalt must be distinguished by the presence of a distinct shake-up satellite structure in  $\text{Co}^{2+}$ , arising from the presence of unpaired electrons in its valence orbital [24].  $\text{Co}^{3+}$  is almost always in a low spin state, so this effect is absent or very limited. In our results, with increasing cobalt content, the satellite ratio decreased; that is, some oxygen in ceria was incorporated into cobalt to form higher valence state cobalt, which is assumed to be related to the well known oxygen storage function of ceria. These results indicate that ceria provides oxygen to cobalt, which retains its higher valence state with increasing Co content, leading to a coexistence of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ .

Figure 5 shows the field dependence of room-temperature magnetization for  $\text{CeO}_2$  powder with various Co contents. The undoped sample shows a similar hysteresis loop to that of the single-crystal powder (inset of figure 5). Clearly, this very small magnetization also results from the oxygen vacancy induced in the grinding process. However, well defined hysteresis loops and larger magnetization were observed in Co doped  $\text{CeO}_2$  samples. Initially the magnetization of  $\text{Ce}_{1-x}\text{Co}_x\text{O}_2$  increases with Co content, but when  $x$  increases beyond 4% a surprising inverse correlation between the saturation magnetization and Co content was observed. A mixture behaviour of FM and paramagnetism (PM) was exhibited in the sample with 1% Co, while saturation of magnetization ( $M_s = 0.47 \text{ emu g}^{-1}$ ) was obtained in 2.1% Co doped  $\text{CeO}_2$ . When given as magnetic moment/Co dopant ion, the  $M_s$  of 2.1% Co doped  $\text{CeO}_2$  is about  $0.5 \mu_B/\text{Co}$ , which is nearly a hundredfold larger than that of the pure single-crystal  $\text{CeO}_2$  powder. This significant enhancement of magnetization can be ascribed to the so-called F-centre exchange coupling (FCE), in which both oxygen vacancies and TM doping are involved [4]. As mentioned above,  $\text{CeO}_2$  itself is prone to form an oxygen vacancy. Furthermore, when a divalent or trivalent Co ion is substituted in  $\text{CeO}_2$ , an oxygen vacancy is naturally formed to ensure charge neutrality. An oxygen vacancy in  $\text{CeO}_2$  traps an electron to



**Figure 6.** Magnetization versus field curves for O<sub>2</sub> and H<sub>2</sub>/Ar annealed 1% Co doped CeO<sub>2</sub> powder.

from F-centres, which with two Co ions constitutes a Co<sup>2+</sup>–□–Co<sup>2+</sup> group, where □ denotes the oxygen vacancy. The electron trapped in the oxygen vacancy occupies an orbital which overlaps the d shells of both Co iron neighbours. The radius of the electron orbital is estimated to be a significant large value of a few tens of nanometres [17]. Based on Hund's rule and the Pauli exclusion principle, spin orientations of the trapped electrons and the two neighbouring Co ions should be parallel in the same direction, thus ferromagnetic ordering is achieved. This oxygen vacancy involving mechanism is further confirmed by the variation of RT-FM observed in an oxygen and H<sub>2</sub> annealed sample, as shown in figure 6. The 1% Co doped CeO<sub>2</sub> powders were annealed under 1 atm of O<sub>2</sub> and H<sub>2</sub>(10%)/Ar(90%), each at 300 °C for 2 h. After O<sub>2</sub> annealing, the samples show little hysteresis loop and the FM signal decreases significantly, while the H<sub>2</sub> annealed sample shows enhanced FM with  $M_s$  of about 0.4 emu g<sup>-1</sup>.

The complex magnetic behaviour of CeO<sub>2</sub> with Co content can be explained by the competition of super-exchange coupling and the FCE coupling. To interpret our results, we suppose that the Co ions are randomly distributed in the CeO<sub>2</sub> host matrix and can be approximately divided into three subsets. One subset of Co is far apart from other Co ions, thus the spins of these isolated Co ions are completely free, and the magnetism follows a simple PM behaviour. As to the second set of ions, Co ions have a smaller separation from each other and they are affected by FCE interactions, leading to a typical FM behaviour. Meanwhile, there must also be some Co ions that have nearest neighbour Co ions (named paired Co) [9]. The paired Co ions (mediated by one oxygen ion) are expected to have super-exchange interaction with nearest neighbour Co ions thus giving rise to an antiferromagnetic behaviour. In this physical picture, when the Co content is small (e.g. 1%), the first and second subsets of Co ions dominantly coexist, thus a mixture behaviour of PM and FM is observed. As Co content increases, more Co ions are mediated by FCE interaction due to the smaller distance between Co ions and the increase of concentration of oxygen vacancies. Therefore, an increase of magnetization with Co content is reasonably observed in the CeO<sub>2</sub>. However, with further increasing of Co content, the number of the third subset of Co ions increases and the antiferromagnetic interactions quickly reduce the FM of the doped CeO<sub>2</sub> powder. Clearly, a competition between the magnetic properties resulting from three subsets of Co ions underlies the complex magnetic behaviour in Co doped CeO<sub>2</sub> powders.

#### 4. Conclusion

In summary, the observation of RT-FM in pure and Co doped CeO<sub>2</sub> powder has given a strong evidence of oxygen vacancy induced ferromagnetic ordering in these supposedly nonmagnetic oxide hosts. The pure single-crystal CeO<sub>2</sub> powder exhibits a weak but unambiguous RT-FM, which was proved theoretically and experimentally to be originated from oxygen vacancies. A slight Co doping in CeO<sub>2</sub> causes a nearly two-orders enhancement of magnetism to 0.47 emu g<sup>-1</sup> as compared with the pure sample. This strong RT-FM was well interpreted by the F-centre exchange coupling mechanism, in which both oxygen vacancies and magnetic ions are involved. Our results indicate that the large magnetic moment recently found in semiconductor or insulating oxide, at least partly, originates from a combination effect of oxygen vacancies and TM doping. A first-principle calculation on this combination effect is ongoing and will be reported elsewhere.

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