Large Curie Temperatures for Co doped $CeO_{2-\delta}$: can we explain them?

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Workshop on Novel Methods for Electronic Structure Calculations, La Plata October 2009

Diluted magnetic oxides (DMOs)

- Search for RT-FM materials (not new)
- DMOs obtained by doping oxide matrix with TM ions
- Pioneering works of Dietl et al (Mn doped ZnO), RT ferromagnetism observed in various doped oxide hosts (among others TiO_2).
- Samples sensitive to preparation methods and growth conditions.
- Ferromagnetism seems to be linked to structural defects and to the presence of oxygen vacancies.
- Not obvious link between conduction and FM behaviour.
- For spintronic applications: critical T's above room temperature are critical.

Co-doped CeO_2

- Ceria is a transparent, high dielectric constant, rare earth oxide, whose fluorite structure matches well with silicon

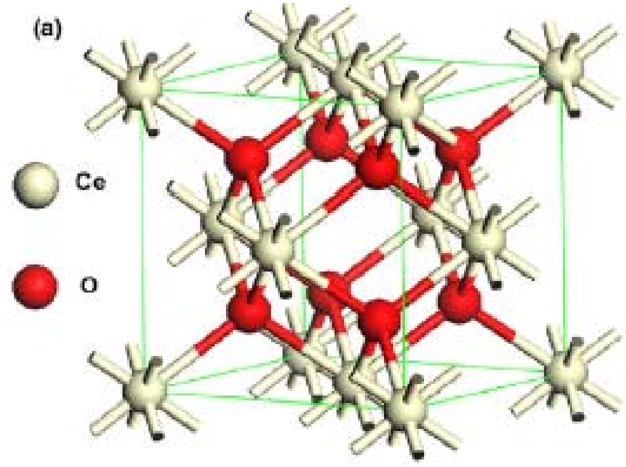
- Ferromagnetic behavior observed well above RT even for low Co-doping concentration.

- Keeps fluorite structure under doping and upon formation of oxygen vacancies: promises good integrability for spintronic devices.

- Controversy regarding critical T’s and magnetic moments’ values as a function of doping concentration. Wide range of magnetic moments has been reported.

- There are some concerns about the intrinsic nature of ferromagnetism.

CeO_2



FluoriteStructure

Some experimental results for Co doped Ceria

PHYSICAL REVIEW B **75**, 121304(R) (2007)

Room temperature ferromagnetism in Co-doped CeO_2 films on Si(001)

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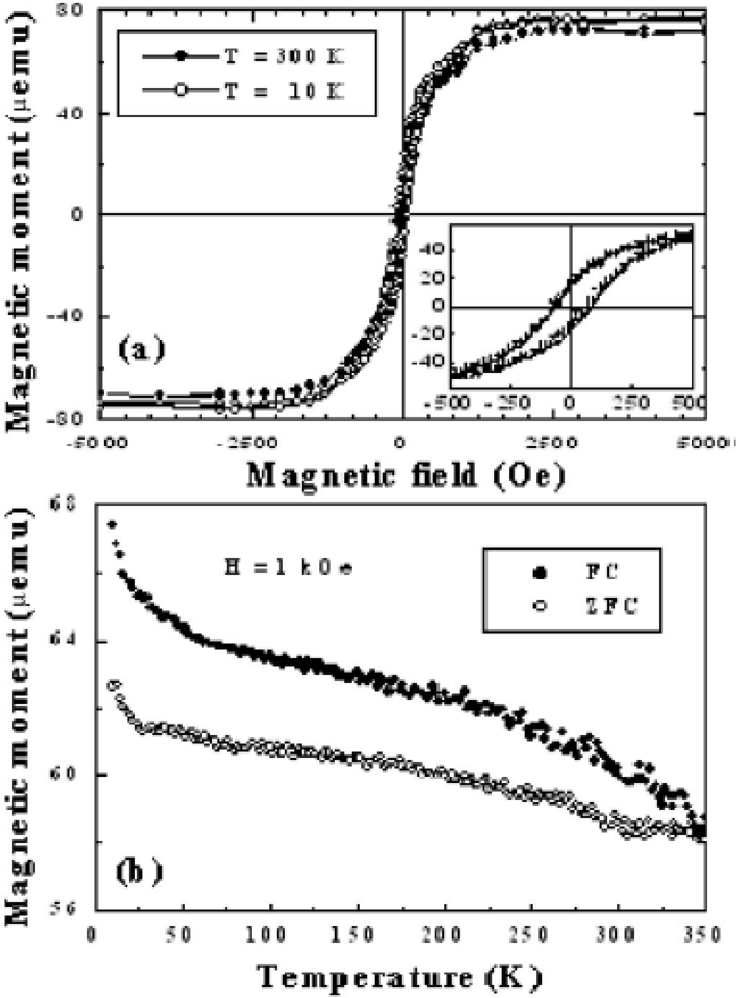

FIG. 4. (a) Hysteresis loops measured for CeO_2 film with 13.2 at. % Co. The inset shows the inner part of the loops. (b) FC and ZFC curves indicating a ferromagnetic state with critical temperature above 350 K.

APPLIED PHYSICS LETTERS **88**, 142511 (2006)

Ferromagnetism in Co doped CeO$_2$: Observation of a giant magnetic moment with a high Curie temperature

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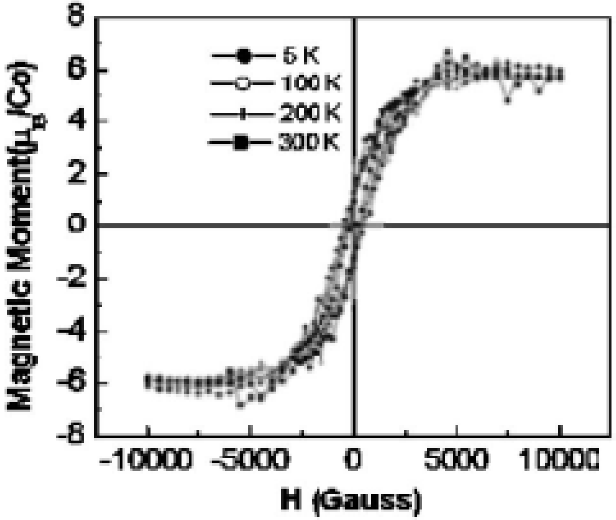
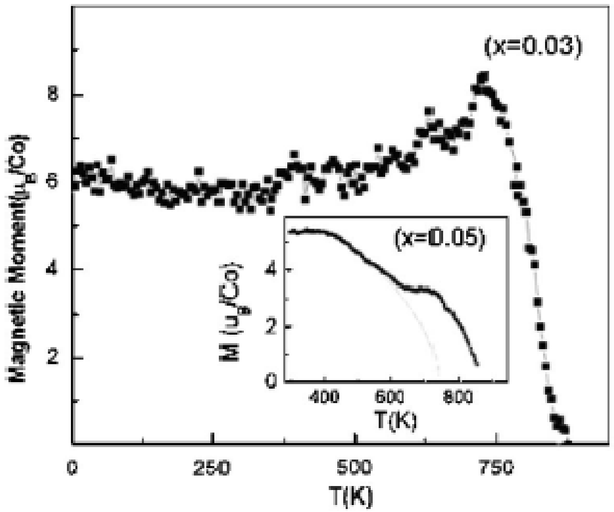


FIG. 3. Magnetization loop (M vs H) for Ce$_{0.97}$Co$_{0.03}$O$_{2-\delta}$ at different temperatures.



4. Saturation magnetization as a function of temperature for Co$_{0.03}$O$_{2-\delta}$. The inset shows the magnetization of the Ce$_{0.95}$Co$_{0.05}$O$_{2-\delta}$ s a function of temperature.

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Room-temperature ferromagnetism in pure and Co doped CeO_2 powders

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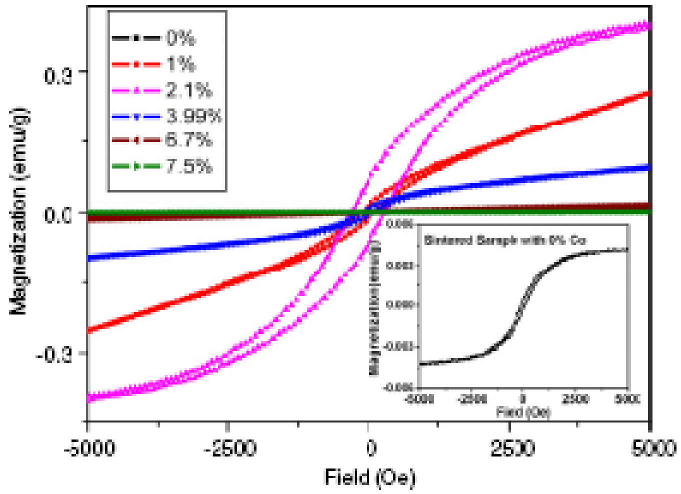

Figure 5. Magnetization versus magnetic field curves for the Co doped CeO_2 at room temperature. Inset is the enlarged M–H curve of undoped CeO_2.

Room temperature ferromagnetism of Co doped $CeO_{2-\delta}$ diluted magnetic oxide: Effect of oxygen and anisotropy

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Structural defects seem
to have no effect on
The magnetic properties.

Presence of oxygen
during growth or annealing
reduces drastically
ferromagnetism.

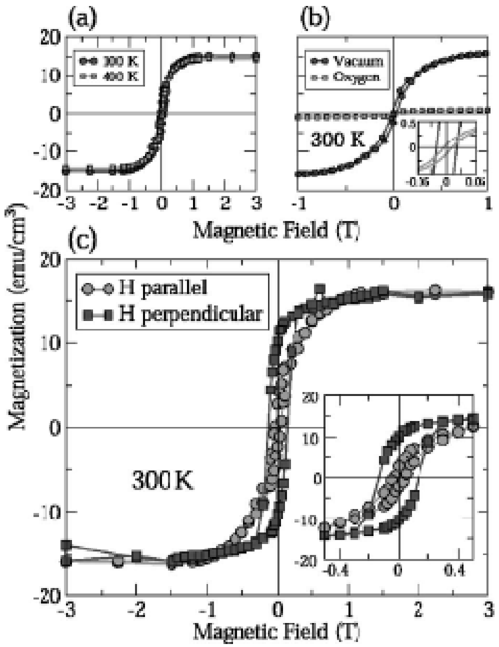

FIG. 2. (a) Magnetization cycles (in plane magnetic field) as a function of temperature obtained for a 4.5% Co doped $CeO_{2-\delta}$ film deposited on Si. (b) Magnetization cycles (in plane magnetic field) for a 4.5% Co doped $CeO_{2-\delta}$ film grown under vacuum and under oxygen rich conditions on Si. (c) Magnetization cycles (in plane and out of plane magnetic fields) of a 4.5% Co doped $CeO_{2-\delta}$ film epitaxied on $SrTiO_3$. Measurements displayed in (a) and (c) were performed with a SQUID and the curves in (b) were obtained using AGFM.

Tc> 400K

Grown on Si, no anisotropy

Grown on SrTiO3 strong,
Perpendicular anisotropy

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Structural, magnetic and spectroscopic study of a diluted magnetic oxide: Co doped $CeO_{2-\delta}$

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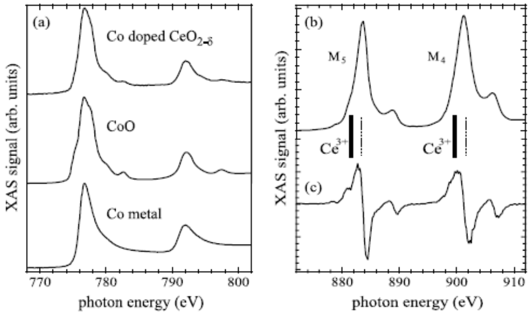

Figure 6. (a) CoL_2–L_3 XAS spectra of 4.5% Co doped $CeO_{2-\delta}$, CoO and Co. (b) M_4–M_5 XAS spectrum of Co doped $CeO_{2-\delta}$ grown on Si. (c) Derivative of the absorption spectra depicted in (b).

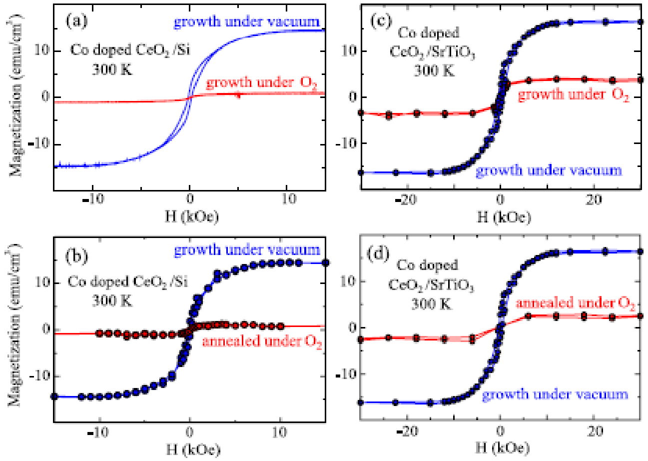

Figure 4. (a) Magnetization cycles measured with AGFM (in-plane magnetic field) at 300 K obtained for a 4.5% Co doped $CeO_{2-\delta}$ film deposited on Si for samples grown under vacuum and under oxygen-rich conditions. (b) Magnetization cycles (in-plane magnetic field) measured with a SQUID magnetometer at 300 K obtained for a 4.5% Co doped $CeO_{2-\delta}$ film deposited on Si under vacuum before and after annealing under oxygen-rich conditions. (c), (d) The same as (a), (b) for epilayers grown on $SrTiO_3$(001) (SQUID).

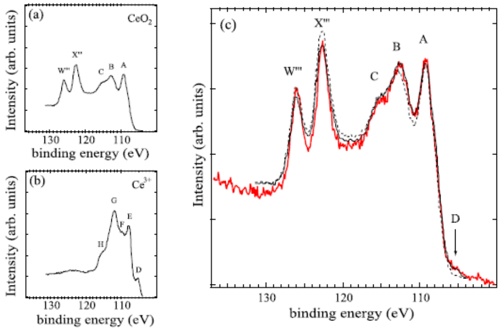

Figure 7. (a) XPS spectrum of CeO_2 in the Ce 4d spectral region. (b) XPS spectrum of Ce^{3+} in the Ce 4d spectral region. (Parts (a) and (b) adapted from [37] with permission from Elsevier.) The characteristic spectral features in (a) and (b) are labeled with the same nomenclature as used in [37]. (c) Thick red (gray) line, Ce 4d XPS spectrum of Co doped $CeO_{2-\delta}$ grown on Si; thin black dashed line, scaled CeO_2 spectrum; thin black line, linear combination of the spectra in (a) and (b).

B.Vodungho, F.Vidal et al, J.Phys: Condensed Matter 20, (2008), 125222

Charge compensation mechanisms

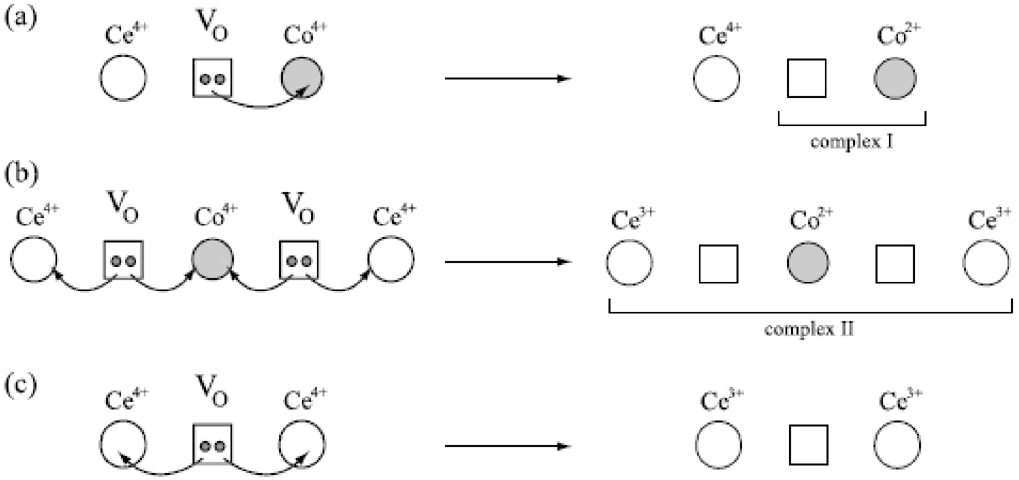

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Figure 9. (a) Scheme illustrating the formation of complex I (see the text for details). (b) The same as (a) for complex II. (c) Scheme illustrating the formation of Ce^{3+} ions when an oxygen vacancy is created in the CeO_2 lattice.

*- Skorodumova N V, Simak S I, Lundqvist B I, Abrikosov I A and Johansson B 2002 *Phys. Rev. Lett.* 89 166601

In this work we study

- Role played by oxygen vacancies on the magnetic properties of a bulk Ceria matrix as a function of homogeneously distributed Co impurities.
- We take into account the presence of Ce^{3+} in the relaxation processes.
- Follow the evolution of the magnetic interactions with the number of oxygen vacancies per Co (not yet reported in the literature)

LSDA and LSDA + U
calculations.

Some calculation details

- DFT calculations within LDA using Wien2k[1]
- R_{MT}= 1.9 Bohr for Co, 1.6 for O and 2.3 for Ce.
- RKmax=7 (6 for the biggests cells). (APW +lo)
- 7x7x7 k-mesh for x_{Co}= 12.5 % and 5x5x5 for 6.25%.
- Relaxations are done with localized 4f states treated as core levels.
- In the LSDA+U calculations, U_{eff}= 6eV (ref 2 and 3)

1 *J.P.Perdew and Y.Wang, Phys Rev B 45, 13244 (1992)*

2 *V.Anisimov et al , Phys Rev B 48, 16929 (1993)*

3 *D.Andersson et al, Phys Rev B 75, 035109 (2007)*

CeO_2

Fluorite structure

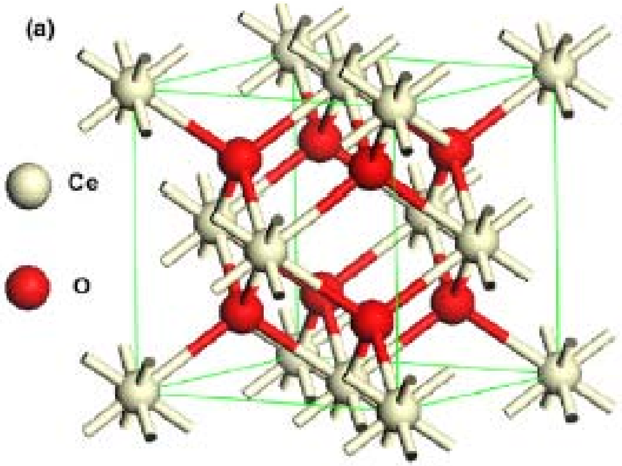
Experimental lattice parameter: 5.411 A

Each Ce^{4+} coordinated to 8 oxygens

O^{-2} ions tetrahedrally coordinated to the Ce^{4+} ions

Minor lattice constant changes and preservation of cubic symmetry upon doping.

We consider the experimental lattice constant of unreduced Ceria in the calculations. Internal relaxations are undertaken .

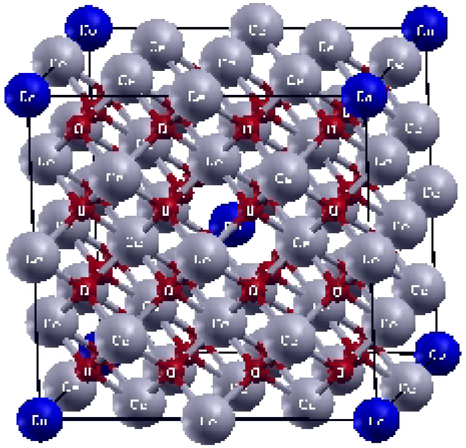


Supercell calculations: Co doped Ceria

For x= 6.25%

Co-Co distance= 7.65 A

2x2x2 BCC

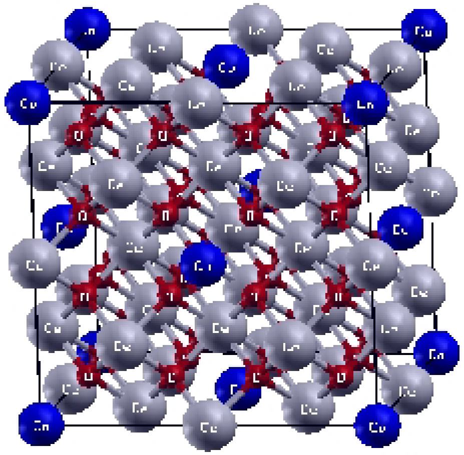


Stoichiometric compound:
48 atoms

For x= 12.5%

Co-Co distane= 9.37 A

2x2x2 FCC



Stoichiometric compound:
24 atoms

**For each Co concentration:
zero, one and two vacs.
per Co are considered**

Location of oxygen vacancies
in Co doped Ceria.

One vacancy per Co

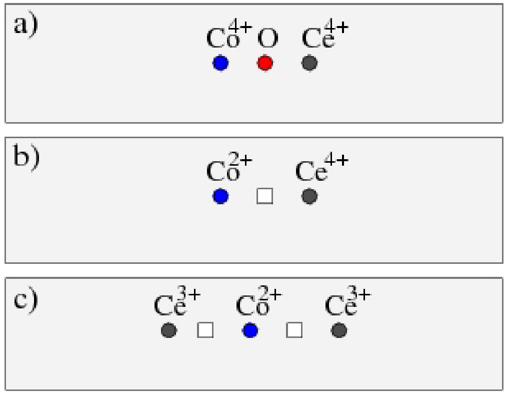
X= 12.5%

Oxygen vacancy nearest neighbor to Co and far from Co are considered.

After relaxation

Difference in energy= 0.55 eV per Co in favor of vacancy near the impurity.
Left behind electrons go to Co (Co2+).

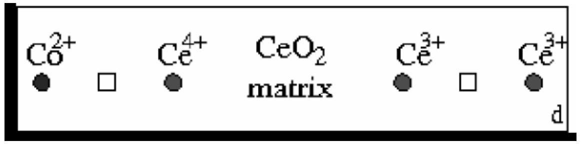
Co nucleates oxygen vacancies



Two vacancies per Co

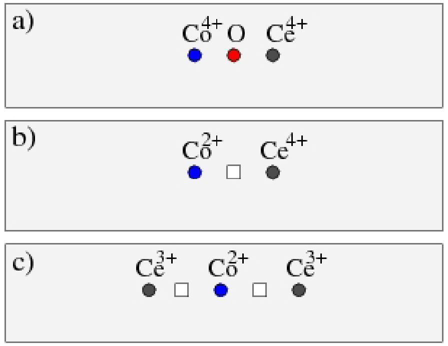
X= 6.25%

Two vacancies near Co and
one vacancy near Co and the other far away are being considered.



After relaxation,
Energetically favored: 2 vacs near Co by 0.62 eV.

Ionic relaxation



Zero oxygen vacancies per Co.

Co and Ce in +4 state. No 4f localization.
The 8 oxygen atoms nn to Co move towards it (0.09 A for x= 6.25%).
Nearest Ce atoms move towards Co by 0.04 A.

One Oxygen vacancy per Co

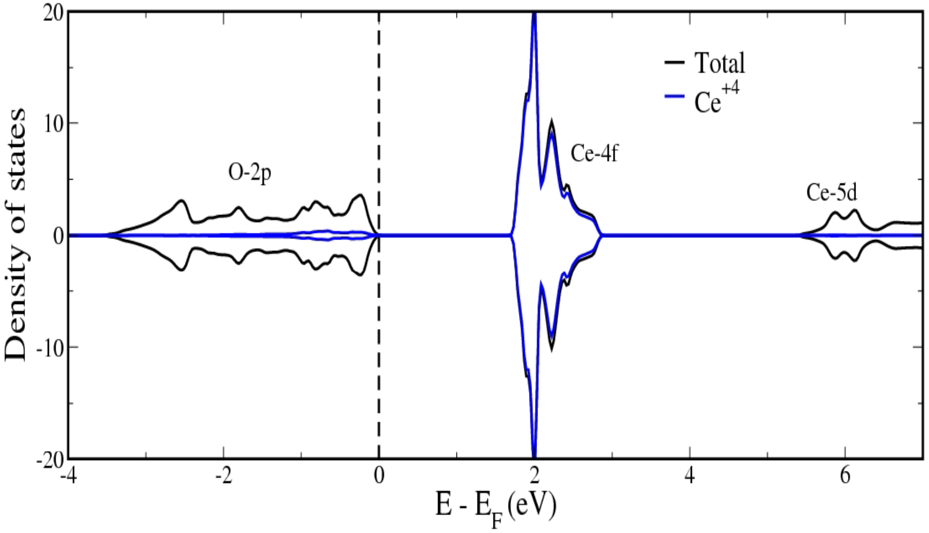
No 4f localization.
Nearest neighbor Ce and Co ions move outwards from vac (0.1A and 0.28 A respectively).
Nearest neighbohr oxygen atoms move 0.15 A towards de vacancy and 0.06 A towards the impurity.

Two oxygen vacancies per Co

Important relaxation. The oxygen atoms nn to Co move towards it and away from Ce $^{3+}$

Magnetic coupling and electronic structure as a function of Co doping and reduction

Total and local Ce 4f densities of states for pure CeO_2



Non-magnetic
Insulator

LSDA calculation

Electronic structure of Co doped Ceria x= 6.25%

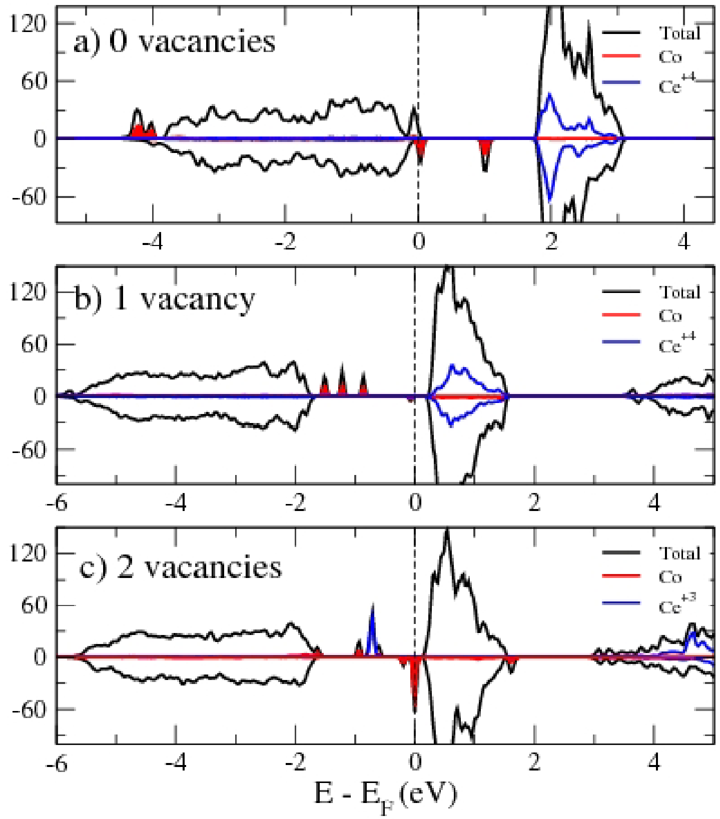
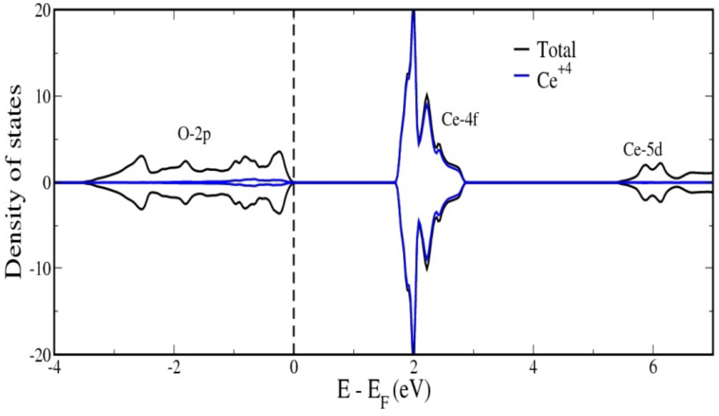


Figure 4: Density of states for $Ce_{1-x}Co_xO_{2-\delta}$ with x= 6.25% with a) unreduced system (δ=0), b) one vacancy per Co (δ=0.0313), and c) two vacancies per Co (δ=0.0625). Total DOS (black), partial DOS for Cobalt (red) and Cerium (blue). In a) and b), there is no charge localization on any Ce site. In c) the partial DOS of a Ce^{+3} is shown.

Co Impurity peaks at the bottom of majority valence band.
Majority peak at valence band top: due to oxygen atoms nn of the impurity.

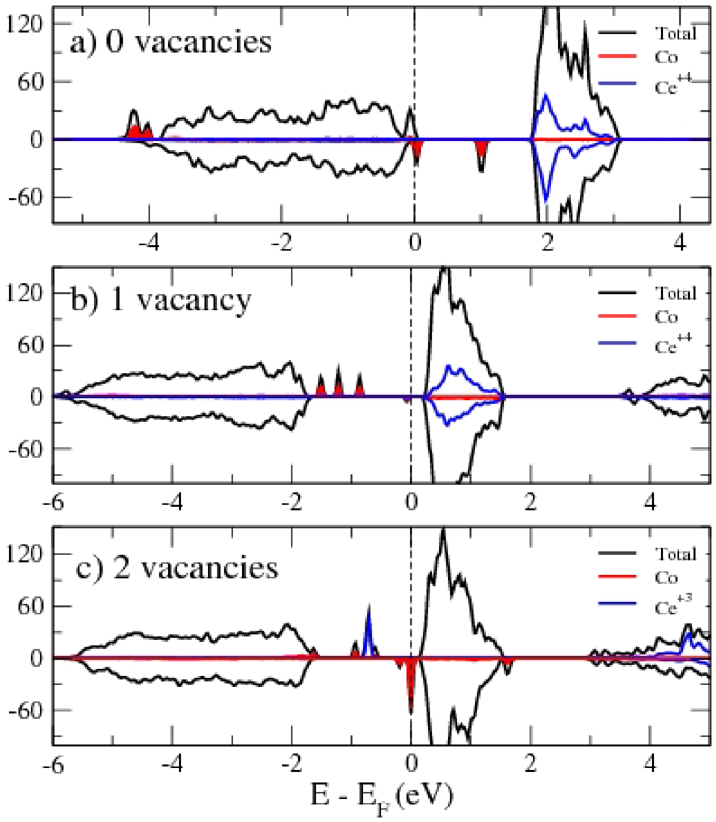
Majority Co impurity peaks shift towards Ceria's gap.
Fermi level lies in localized Co minority peak, which is now near the 4f empty states..

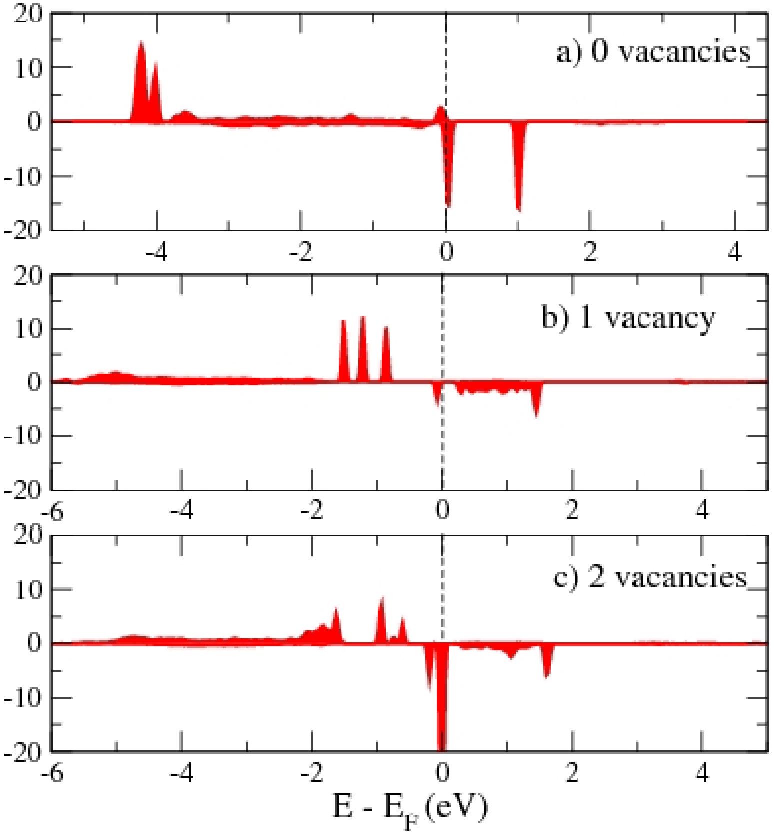
Localization of extra charge on the 4f Ce^{+3} orbital.



CeO_2

Local density of states on Co impurity site. X=6.25%





Electronic structure Co doped Ceria X= 12.5 %

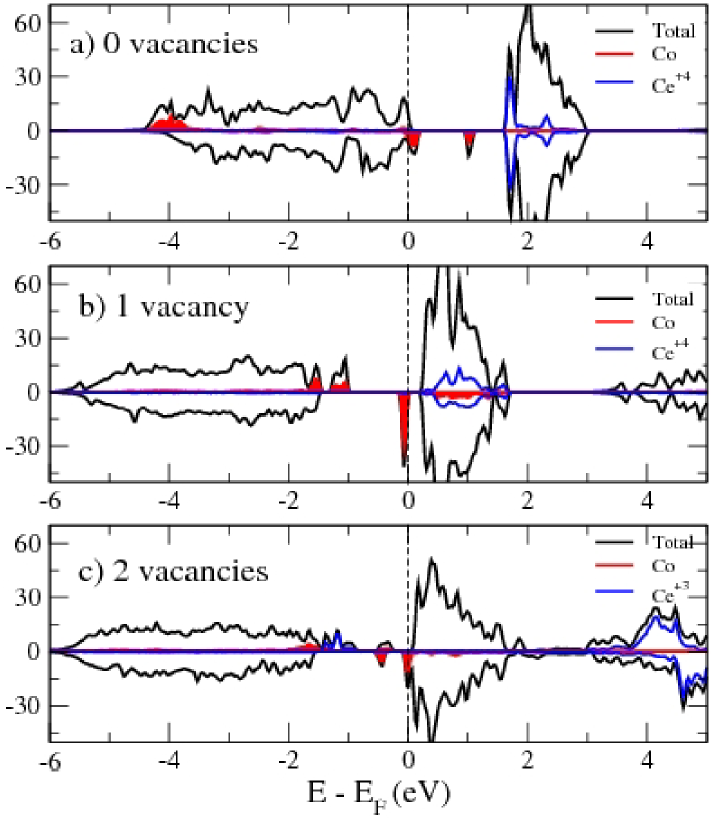
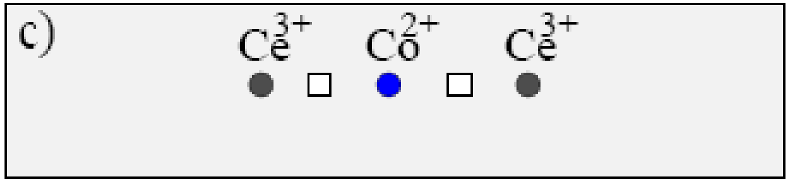


Figure 5: Density of states for $Ce_{1-x}Co_xO_{2-\delta}$ with x= 12.5% with a) unreduced system (δ=0), b) one vacancy per Co (δ=0.0625), and c) two vacancies per Co (δ=0.125). Total DOS (black), partial DOS for Cobalt (red) and Cerium (blue). In a) and b), there is no charge localization on any Ce site. In c) the partial DOS of a Ce^{+3} is shown.

Magnetic coupling between Co and Ce^{+3}

This coupling takes place when two vacancies per Co are present

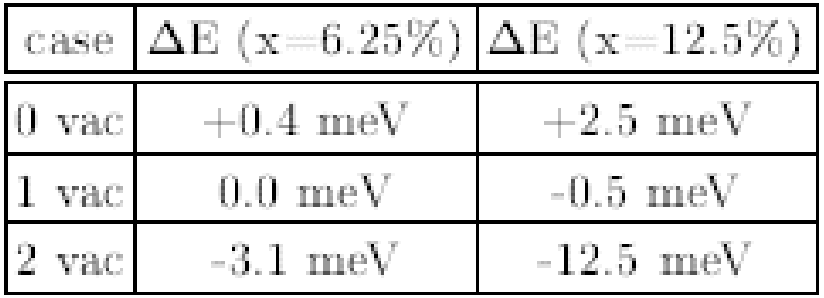


We consider the case x= 12.5%.

Compare FM and AFM relative spin alignments of Co and Ce+3

$\Delta E = E_{AFM} - E_{F=}$ =120 meV per Co ion ***Strong ferromagnetic coupling.***

Magnetic coupling among dopants



case	ΔE (x=6.25%)	ΔE (x=12.5%)
0 vac	+0.4 meV	+2.5 meV
1 vac	0.0 meV	-0.5 meV
2 vac	-3.1 meV	-12.5 meV

Table I: ΔE = E_F - E_{AF}, energy difference between FM and AF per Co ion to estimate the magnetic coupling between Co atoms.

Without vacancies= For both impurity concentrations, Co-Co nn ions slightly AF

Oxygen vacancies= tendency towards ferromagnetic alignment appears
with increasing number of vacancies.

Energy differencies obtained do not explain the large Curie temperatures of the experiments. Direct exchange does not underly this phenomena, other mechanisms.

[redacted]

PHYSICAL REVIEW B **79**, 100403(R) (2009)

Recently

Oxygen-vacancy-induced ferromagnetism in CeO_2 from first principles

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The electronic and magnetic properties of CeO_2 with various concentrations of oxygen vacancies have been studied by first-principles calculations within the LSDA+U method and were found to remarkably depend on the oxygen vacancy concentration. With increasing oxygen deficiency, the electrons left behind by oxygen removal not only localize on Ce 4f orbitals but also on the vacancy sites. This leads to the magnetic mechanism with both superexchange and polarization in the cases of heavy doping, effectively enhancing the stability of ferromagnetism. The study reveals the magnetic properties and associated magnetic mechanisms of CeO_2 with the different oxygen deficiencies.

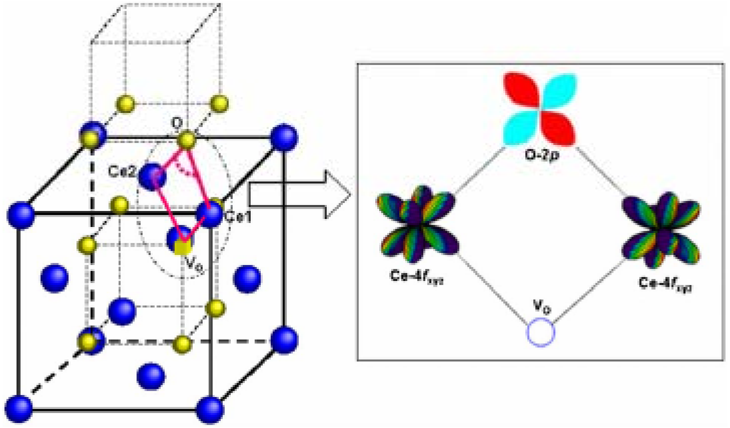

FIG. 3. (Color online) Schematic for the superexchange interaction between two reduced Ce ions. Ce1 and Ce2 represent the two reduced Ce ions. The Ce1-O-Ce2 superexchange is responsible for both light- and heavy-doping cases, while the interaction between Ce1 and Ce2 via V_O is effective only for the heavy-doping case.

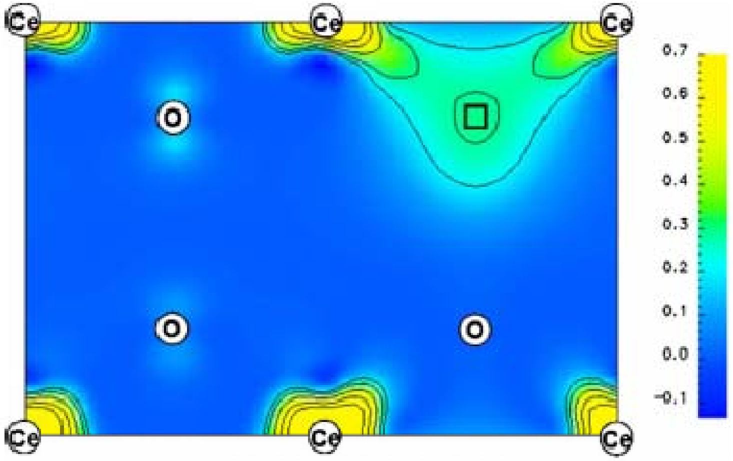

FIG. 2. (Color online) The charge-density analysis of the gap state in Fig. 1(d). The (110) plane through the two reduced Ce ions and O vacancy is chosen, and oxygen vacancy is represented as the solid square. The contour goes from 0.2 to 0.6 $e/Å^3$ in intervals of 0.1 $e/Å^3$.

Evolution of magnetic spin moments

X= 6.25

	μ_T	μ_{Co}	μ_O^{nn}	$\mu(Co+O^{nn})$	$\mu(Ce')$
0 vac	$4.76\mu_B$	$2.94\mu_B$	$1.28\mu_B$	$4.22\mu_B$	$0.04\mu_B$
1 vac	$3.00\mu_B$	$2.50\mu_B$	$0.42\mu_B$	$2.92\mu_B$	$-0.17\mu_B$
2 vac	$5.00\mu_B$	$2.49\mu_B$	$0.37\mu_B$	$2.86\mu_B$	$1.9\mu_B$

Upon reduction the effective Co valence goes from +4 to +2 : this is revealed by the decrease in the magnetic moment per Co ion.

X=12.50

	μ_T	μ_{Co}	μ_O^{nn}	$\mu(Co+O^{nn})$	$\mu(Ce')$
0 vac	$4.6\mu_B$	$2.9\mu_B$	$1.28\mu_B$	$4.18\mu_B$	$0.04\mu_B$
1 vac	$3.0\mu_B$	$2.5\mu_B$	$0.40\mu_B$	$2.90\mu_B$	$-0.03\mu_B$
2 vac	$5.0\mu_B$	$2.41\mu_B$	$0.40\mu_B$	$2.81\mu_B$	$1.98\mu_B$

There is almost no difference with Co doping concentration due to strong localization

Magnetic moment per cell depends on degree of reduction

Conclusions

Co doping without vacancies shows slight AFM tendency.

Oxygen vacancies clearly drive ferromagnetic coupling among Co dopant impurities In Ceria.

Oxygen vacancies nucleate in the neighborhood of Co ions,

Reduction increases the localization of the dopant magnetic moments.

The magnetic moment of Co is nearly independent of dopant concentration.

Ce^{+3} and Co are strongly ferromagnetically coupled. They provide the large moments within the ‘cloud’ of the impurities.

Ferromagnetic coupling among impurities decreases with decreasing Co concentration (inhomogeneous distribution?).

Room temperature ferromagnetism cannot be explained by these couplings
(Other mechanisms: Ferromagnetic polarons? Chains of vacancies???? Percolation of complexes?

BUT

The large observed magnetic moments can be attributed to complexes built by Co, Ce^{+3} and oxygen vacancies like the ones treated in this work.