

Morphology, structure and interface properties in metal/oxide systems

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overview

1. cerium oxide ultrathin films on Pt(111) + growth of Ag nanoparticles

- introduction
- morphology, composition and structure
- the CeO₂/Pt interface

2. the Fe/NiO interface

- introduction
- depth-resolved magnetic characterization by NRS

cerium oxide

store, transport and release oxygen

oxydizing
conditions



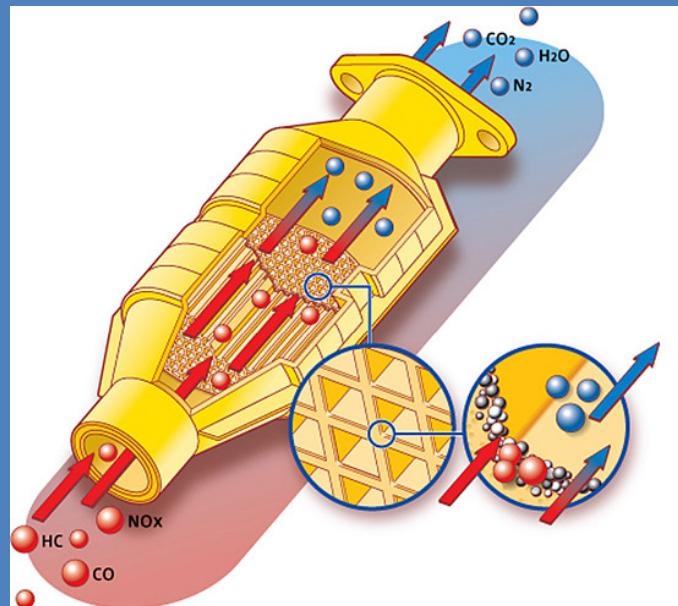
reducing
conditions

A detailed periodic table showing atomic numbers, symbols, and atomic masses for all elements from hydrogen to lanthanides and actinides. The table highlights the s-block (groups 1-2), p-block (groups 13-18), d-block (transition metals), and f-block (lanthanides and actinides). The table includes a legend for phases (Solid, Liquid, Gas) and notes that mass numbers in parentheses are for the most stable isotopes.

Period	Group	Element	Atomic #	Symbol	Atomic Mass
1	1	H	1	H	1.0084
2	2	He	2	He	4.0026
3	3	Li	3	Li	6.941
4	4	Be	4	Be	9.0126
5	5	B	5	B	10.81
6	6	C	6	C	12.011
7	7	N	7	N	14.007
8	8	O	8	O	15.999
9	9	F	9	F	18.998
10	10	Ne	10	Ne	20.179
11	11	Na	11	Na	22.990
12	12	Mg	12	Mg	24.990
13	13	Al	13	Al	26.992
14	14	Si	14	Si	28.086
15	15	P	15	P	30.974
16	16	S	16	S	32.06
17	17	Cl	17	Cl	35.453
18	18	Ar	18	Ar	39.948
19	19	K	19	K	39.098
20	20	Ca	20	Ca	40.08
21	21	Sc	21	Sc	44.956
22	22	Ti	22	Ti	47.88
23	23	V	23	V	50.942
24	24	Cr	24	Cr	51.996
25	25	Mn	25	Mn	54.938
26	26	Fe	26	Fe	55.847
27	27	Co	27	Co	58.933
28	28	Ni	28	Ni	58.69
29	29	Cu	29	Cu	63.546
30	30	Zn	30	Zn	65.39
31	31	Ga	31	Ga	69.72
32	32	Ge	32	Ge	72.39
33	33	As	33	As	74.922
34	34	Se	34	Se	75.96
35	35	Kr	35	Kr	79.904
36	36	Rb	36	Rb	85.468
37	37	Sr	37	Sr	87.62
38	38	Y	38	Y	88.906
39	39	Zr	39	Zr	91.224
40	40	Nb	40	Nb	92.909
41	41	Mo	41	Mo	95.94
42	42	Tc	42	Tc	(98)
43	43	Ru	43	Ru	101.07
44	44	Rh	44	Rh	102.91
45	45	Pd	45	Pd	106.42
46	46	Ag	46	Ag	107.87
47	47	Cd	47	Cd	112.41
48	48	In	48	In	114.82
49	49	Sn	49	Sn	118.71
50	50	Sb	50	Sb	121.75
51	51	Te	51	Te	127.60
52	52	I	52	I	126.91
53	53	Xe	53	Xe	131.29
54	54	Cs	54	Cs	132.91
55	55	Ba	55	Ba	137.33
56	56	to 71	56	to 71	178.49
57	57	Hf	57	Hf	180.95
58	58	Ta	58	Ta	183.85
59	59	W	59	W	186.21
60	60	Re	60	Re	190.2
61	61	Os	61	Os	192.22
62	62	Ir	62	Ir	195.08
63	63	Pt	63	Pt	196.97
64	64	Au	64	Au	200.59
65	65	Hg	65	Hg	204.38
66	66	Tl	66	Tl	207.2
67	67	Pb	67	Pb	208.98
68	68	Bi	68	Bi	209. (210)
69	69	Po	69	Po	209.
70	70	At	70	At	222.
71	71	Rn	71	Rn	
72	72	Rare Earth	72	Rare Earth	
73	73	d-block	73	d-block	
74	74	f-block	74	f-block	
75	75	La	75	La	
76	76	Ce	76	Ce	
77	77	Pr	77	Pr	
78	78	Pm	78	Pm	
79	79	Nd	79	Nd	
80	80	Pm	80	Pm	
81	81	Eu	81	Eu	
82	82	Eu	82	Eu	
83	83	Gd	83	Gd	
84	84	Tb	84	Tb	
85	85	Dy	85	Dy	
86	86	Ho	86	Ho	
87	87	Er	87	Er	
88	88	Tm	88	Tm	
89	89	Yb	89	Yb	
90	90	Lu	90	Lu	
91	91	La	91	La	
92	92	Ce	92	Ce	
93	93	Pr	93	Pr	
94	94	Pm	94	Pm	
95	95	Eu	95	Eu	
96	96	Eu	96	Eu	
97	97	Gd	97	Gd	
98	98	Tb	98	Tb	
99	99	Dy	99	Dy	
100	100	Ho	100	Ho	
101	101	Er	101	Er	
102	102	Tm	102	Tm	
103	103	Yb	103	Yb	
104	104	Lu	104	Lu	
105	105	La	105	La	
106	106	Ce	106	Ce	
107	107	Pr	107	Pr	
108	108	Pm	108	Pm	
109	109	Eu	109	Eu	
110	110	Eu	110	Eu	
111	111	Gd	111	Gd	
112	112	Tb	112	Tb	
113	113	Dy	113	Dy	
114	114	Ho	114	Ho	
115	115	Er	115	Er	
116	116	Tm	116	Tm	
117	117	Yb	117	Yb	
118	118	Lu	118	Lu	
119	119	La	119	La	
120	120	Ce	120	Ce	
121	121	Pr	121	Pr	
122	122	Pm	122	Pm	
123	123	Eu	123	Eu	
124	124	Eu	124	Eu	
125	125	Gd	125	Gd	
126	126	Tb	126	Tb	
127	127	Dy	127	Dy	
128	128	Ho	128	Ho	
129	129	Er	129	Er	
130	130	Tm	130	Tm	
131	131	Yb	131	Yb	
132	132	Lu	132	Lu	
133	133	La	133	La	
134	134	Ce	134	Ce	
135	135	Pr	135	Pr	
136	136	Pm	136	Pm	
137	137	Eu	137	Eu	
138	138	Eu	138	Eu	
139	139	Gd	139	Gd	
140	140	Tb	140	Tb	
141	141	Dy	141	Dy	
142	142	Ho	142	Ho	
143	143	Er	143	Er	
144	144	Tm	144	Tm	
145	145	Yb	145	Yb	
146	146	Lu	146	Lu	
147	147	La	147	La	
148	148	Ce	148	Ce	
149	149	Pr	149	Pr	
150	150	Pm	150	Pm	
151	151	Eu	151	Eu	
152	152	Eu	152	Eu	
153	153	Gd	153	Gd	
154	154	Tb	154	Tb	
155	155	Dy	155	Dy	
156	156	Ho	156	Ho	
157	157	Er	157	Er	
158	158	Tm	158	Tm	
159	159	Yb	159	Yb	
160	160	Lu	160	Lu	
161	161	La	161	La	
162	162	Ce	162	Ce	
163	163	Pr	163	Pr	
164	164	Pm	164	Pm	
165	165	Eu	165	Eu	
166	166	Eu	166	Eu	
167	167	Gd	167	Gd	
168	168	Tb	168	Tb	
169	169	Dy	169	Dy	
170	170	Ho	170	Ho	
171	171	Er	171	Er	
172	172	Tm	172	Tm	
173	173	Yb	173	Yb	
174	174	Lu	174	Lu	
175	175	La	175	La	
176	176	Ce	176	Ce	
177	177	Pr	177	Pr	
178	178	Pm	178	Pm	
179	179	Eu	179	Eu	
180	180	Eu	180	Eu	
181	181	Gd	181	Gd	
182	182	Tb	182	Tb	
183	183	Dy	183	Dy	
184	184	Ho	184	Ho	
185	185	Er	185	Er	
186	186	Tm	186	Tm	
187	187	Yb	187	Yb	
188	188	Lu	188	Lu	
189	189	La	189	La	
190	190	Ce	190	Ce	
191	191	Pr	191	Pr	
192	192	Pm	192	Pm	
193	193	Eu	193	Eu	
194	194	Eu	194	Eu	
195	195	Gd	195	Gd	
196	196	Tb	196	Tb	
197	197	Dy	197	Dy	
198	198	Ho	198	Ho	
199	199	Er	199	Er	
200	200	Tm	200	Tm	
201	201	Yb	201	Yb	
202	202	Lu	202	Lu	
203	203	La	203	La	
204	204	Ce	204	Ce	
205	205	Pr	205	Pr	
206	206	Pm	206	Pm	
207	207	Eu	207	Eu	
208	208	Eu	208	Eu	
209	209	Gd	209	Gd	
210	210	Tb	210	Tb	
211	211	Dy	211	Dy	
212	212	Ho	212	Ho	
213	213	Er	213	Er	
214	214	Tm	214	Tm	
215	215	Yb	215	Yb	
216	216	Lu	216	Lu	
217	217	La	217	La	
218	218	Ce	218	Ce	
219	219	Pr	219	Pr	
220	220	Pm	220	Pm	
221	221	Eu	221	Eu	
222	222	Eu	222	Eu	
223	223	Gd	223	Gd	
224	224	Tb	224	Tb	
225	225	Dy	225	Dy	
226	226	Ho	226	Ho	
227	227	Er	227	Er	
228	228	Tm	228	Tm	
229	229	Yb	229	Yb	
230	230	Lu	230	Lu	
231	231	La	231	La	
232	232	Ce	232	Ce	
233	233	Pr	233	Pr	
234	234	Pm	234	Pm	
235	235	Eu	235	Eu	
236	236	Eu	236	Eu	
237	237	Gd	237	Gd	
238	238	Tb	238	Tb	
239	239	Dy	239	Dy	
240	240	Ho</			

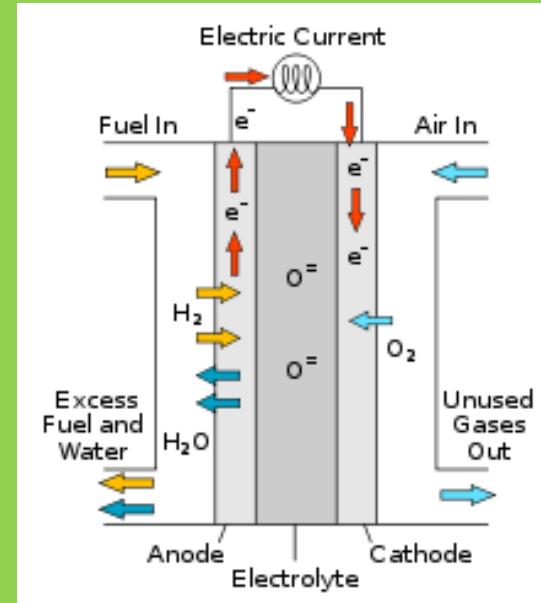
cerium oxide

catalytic converters



- oxidize CO to CO₂
- reduce NO_x to N₂
- self clean from C deposits

solid-oxide fuel cells



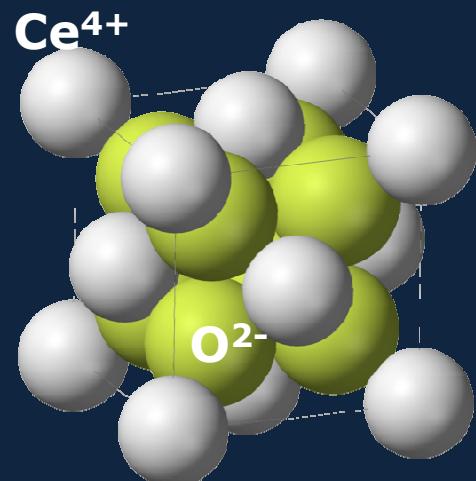
- solid electrolyte
high conductivity for O ions
- production of hydrogen
water gas shift
thermochem. water splitting

cerium oxide

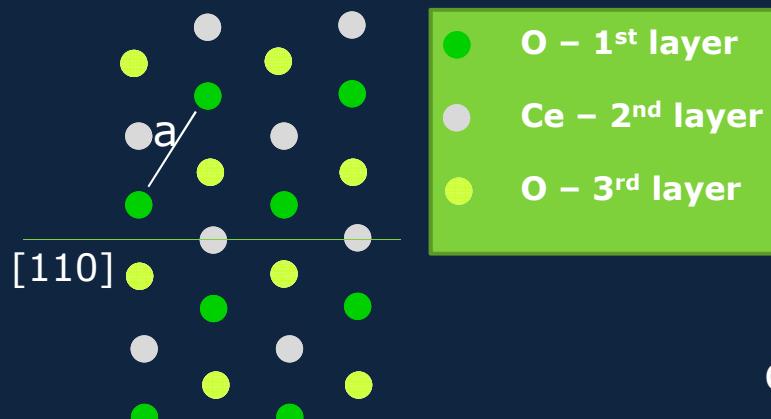
model systems ⇒ understand and optimize
the properties

CeO₂

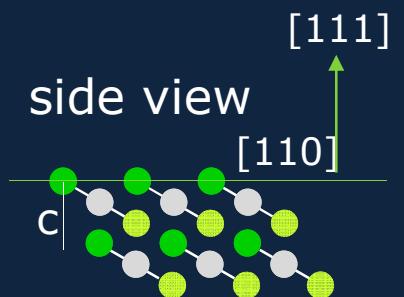
CaF₂ - structure



(111) surface
top view



- O – 1st layer
- Ce – 2nd layer
- O – 3rd layer



$$c_{\text{CeO}_2} = 3.124 \text{ \AA}$$

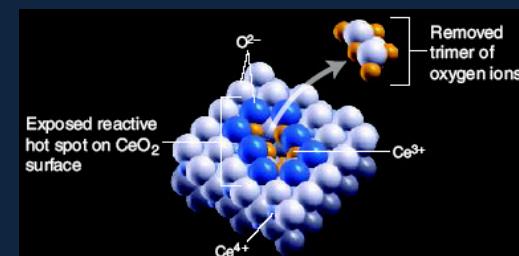
$$a_{\text{CeO}_2} = 3.826 \text{ \AA}$$

previous studies



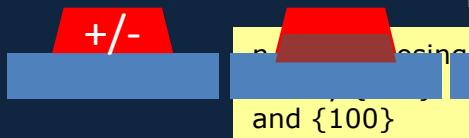
open points

1. oxygen vacancy formation mechanism

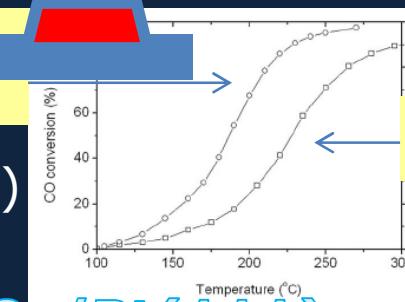


F. Esch et al., Science 309 (2005) 752

2. metal/oxide interaction



3. stabilization of surfaces different from (111)

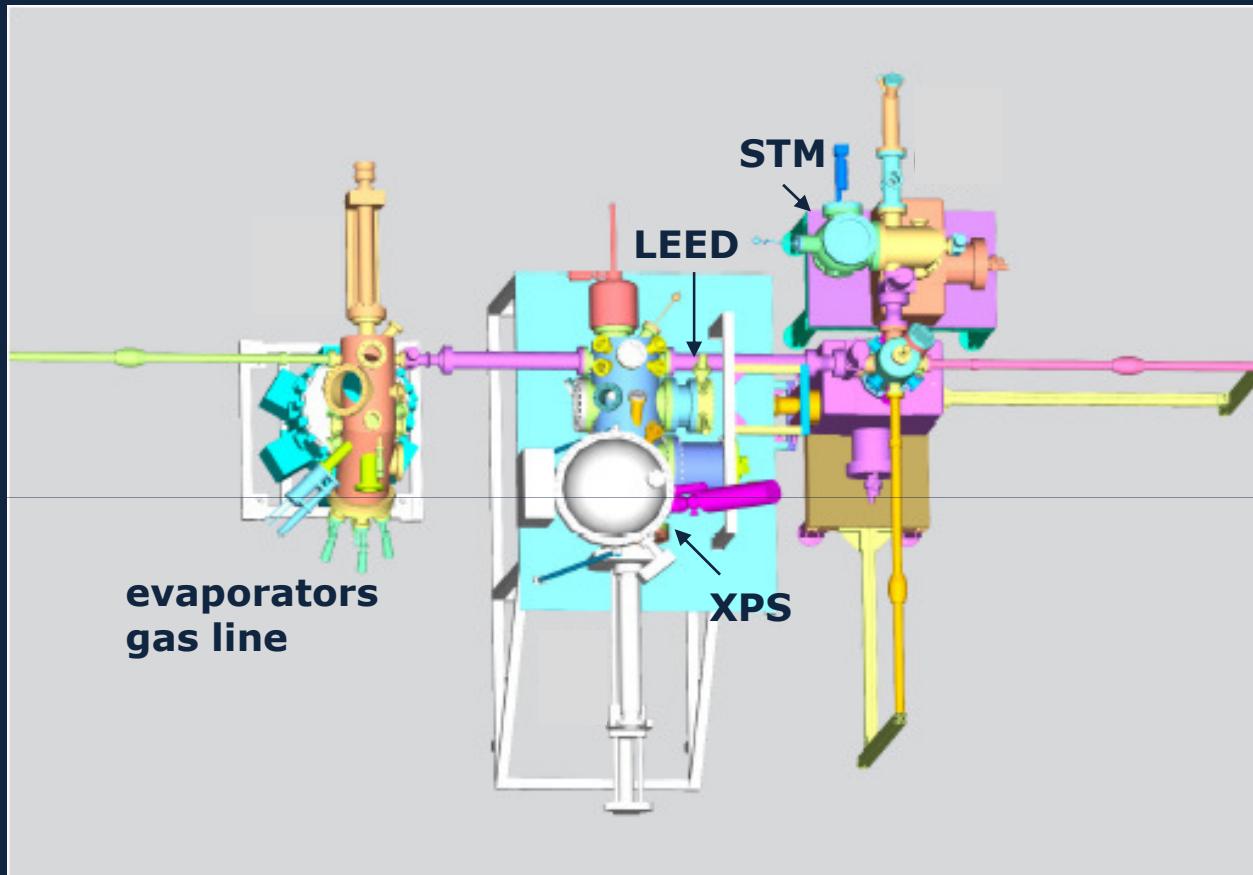


np exposing mainly {111}

⇒ XPS, STM, LEED study of CeO₂/Pt(111)

Zhou et al., J. Cat. 299 (2005) 206

experimental



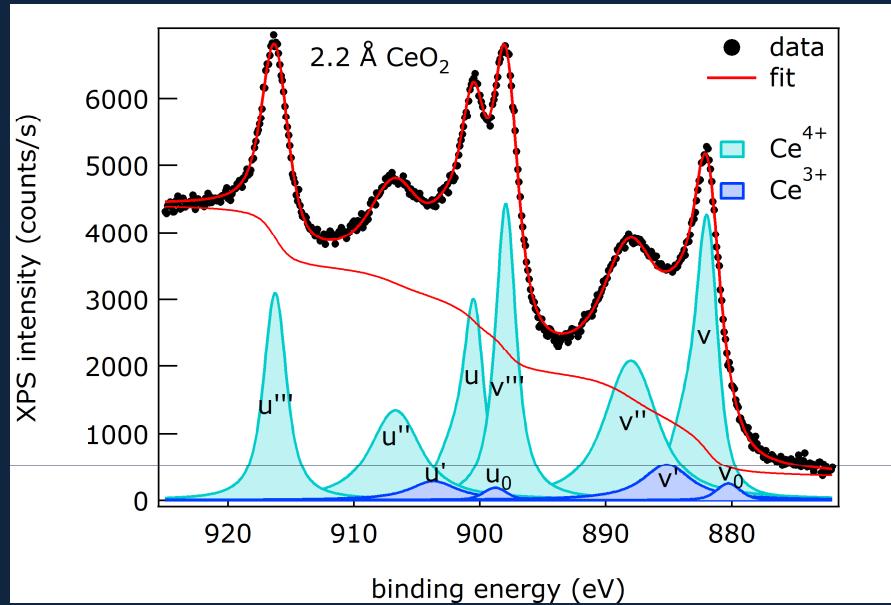
substrate

Pt(111) → $a_{\text{Pt}} = 2.775 \text{ \AA}$ $m = 38\%$
 $a_{\text{CeO}_2} = 3.826 \text{ \AA}$

CeO₂ growth conditions

$R_{\text{Ce}} = 3 \times 10^{-3} \text{ \AA/sec}$ @ RT
 $P_{\text{O}_2} = 1 \times 10^{-7} \text{ Torr}$

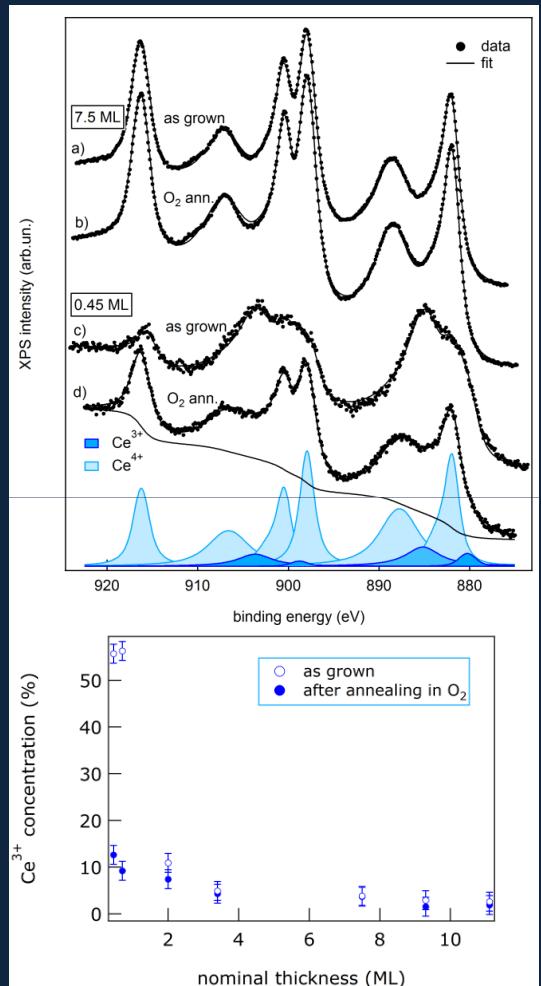
Ce 3d XPS



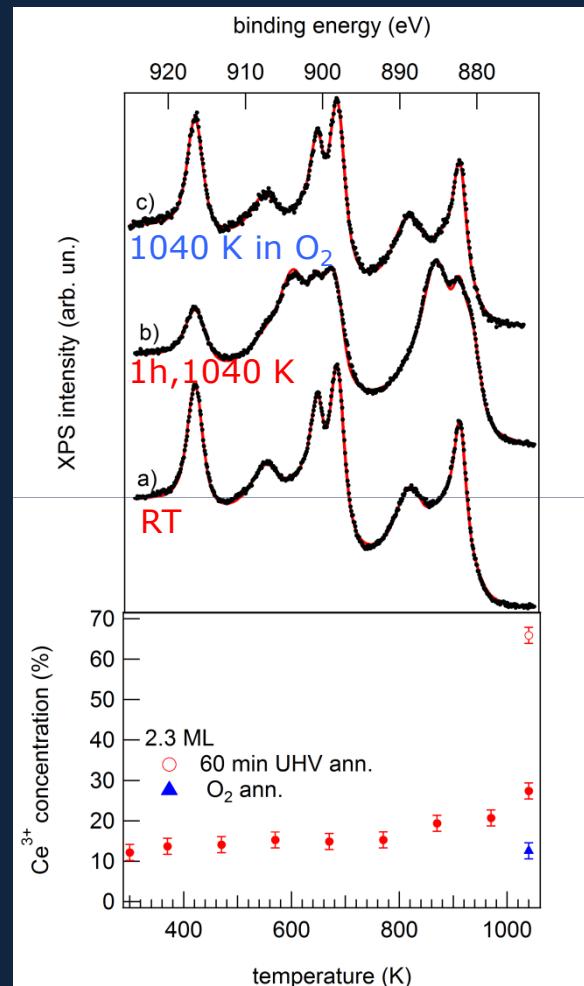
ION	Initial state	Final state	peak
Ce ³⁺	3d ¹⁰ 4f ¹	3d ⁹ 4f ² V ⁿ⁻¹	v ⁰ , u ⁰
	3d ¹⁰ 4f ¹	3d ⁹ 4f ¹ V ⁿ	v', u'
Ce ⁴⁺	3d ¹⁰ 4f ⁰	3d ⁹ 4f ² V ⁿ⁻²	v, u
	3d ¹⁰ 4f ⁰	3d ⁹ 4f ¹ V ⁿ⁻¹	v'', u''
	3d ¹⁰ 4f ⁰	3d ⁹ 4f ⁰ V ⁿ	v''', u'''

stoichiometry

Ce 3d XPS



Ce 3d XPS



annealing @1040 K in O₂
oxidizes the films

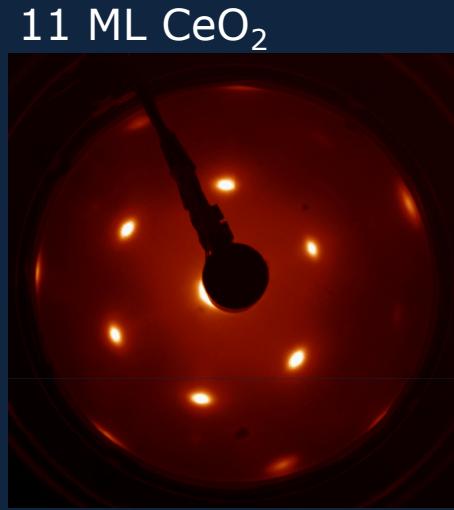
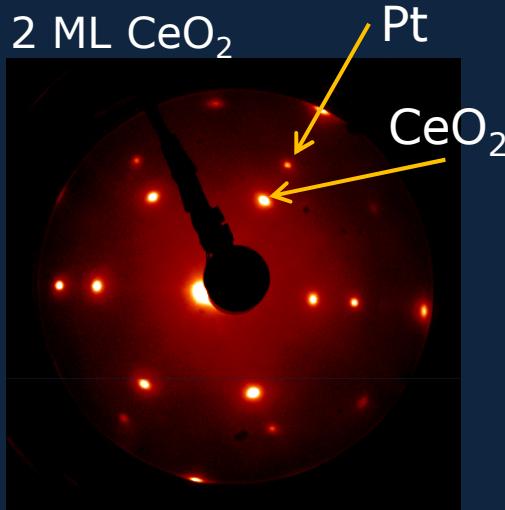
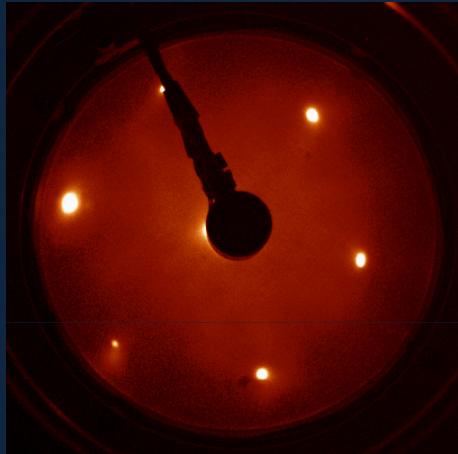
annealing in UHV reduces
the films

structure

LEED

E=80 eV

clean Pt(111)



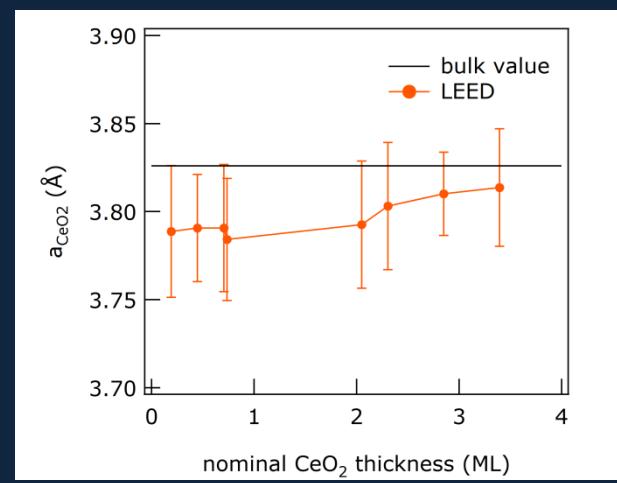
$$a_{\text{CeO}_2} = 3.826 \text{ \AA}$$

$$a_{\text{Pt}} = 2.775 \text{ \AA}$$

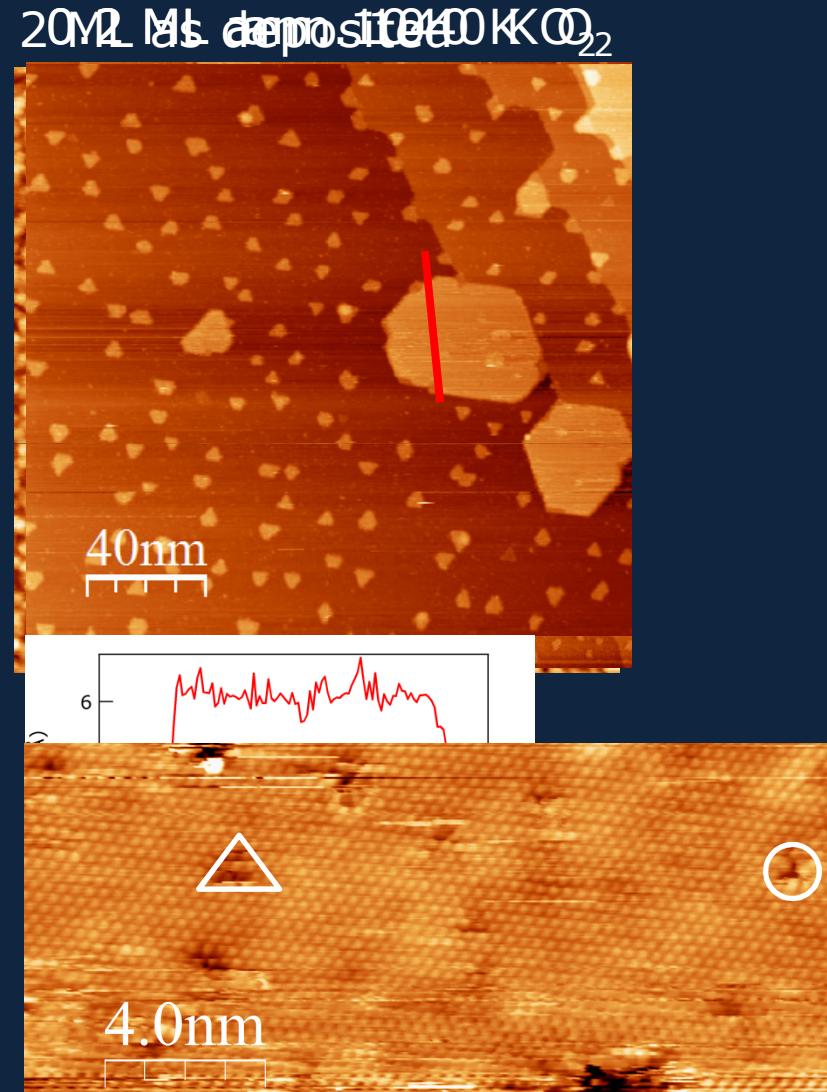
$$m = 38\%$$

epitaxial films

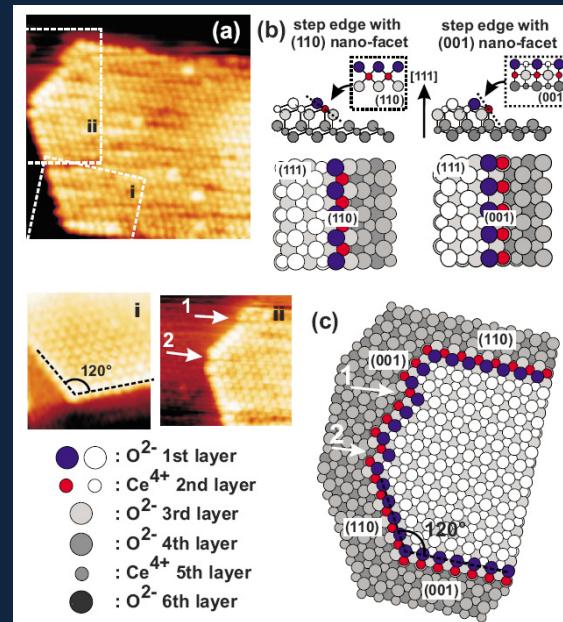
(111) CeO_2
 $<110>_{\text{CeO}_2} // <110>_{\text{Pt}}$



morphology



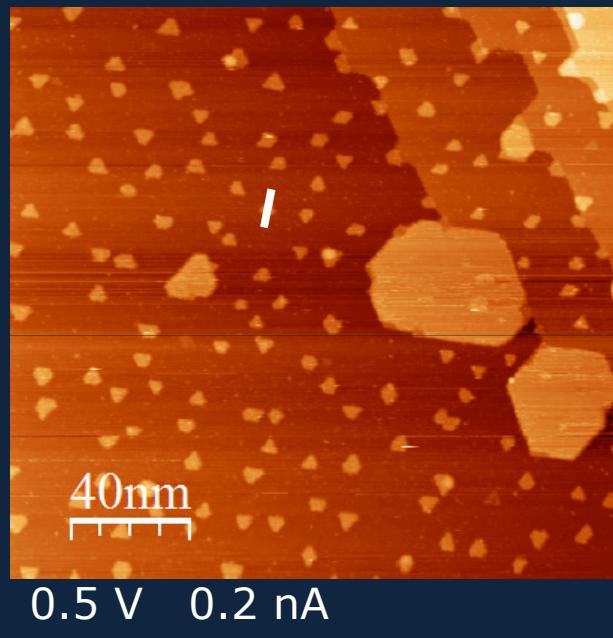
1. Large islands → CeO₂
- 30-50 nm wide
 - 6 Å (2 O-Ce-O ML) high
 - atomically flat
 - preferentially at Pt step edges
 - straight edges, kinks at 120°



S. Torbrügge et al. APL 93 (08) 073112

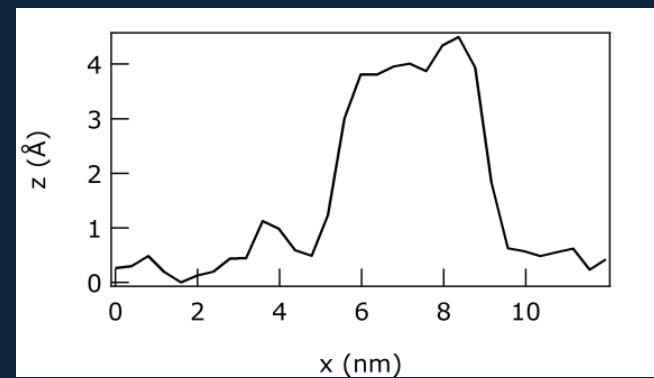
morphology

0.2 ML ann. 1040 K O₂



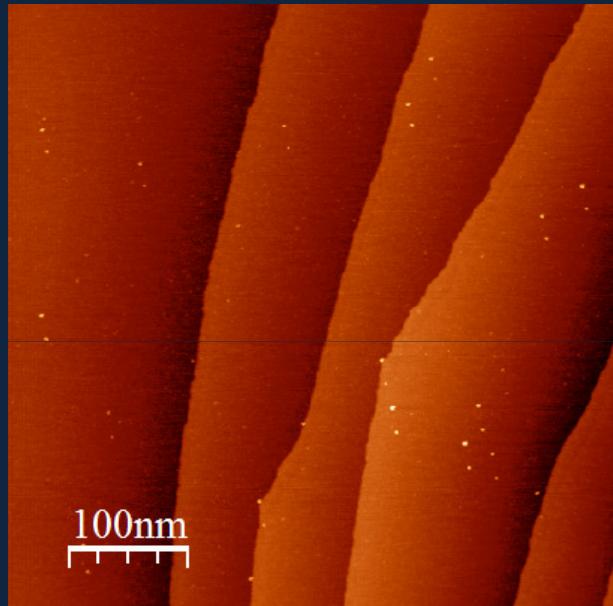
1. Small islands

- ~ 5 nm wide
- ~ 3 Å high
- atomically flat
- uniformly distributed
- triangular shape (kinks at 60°)

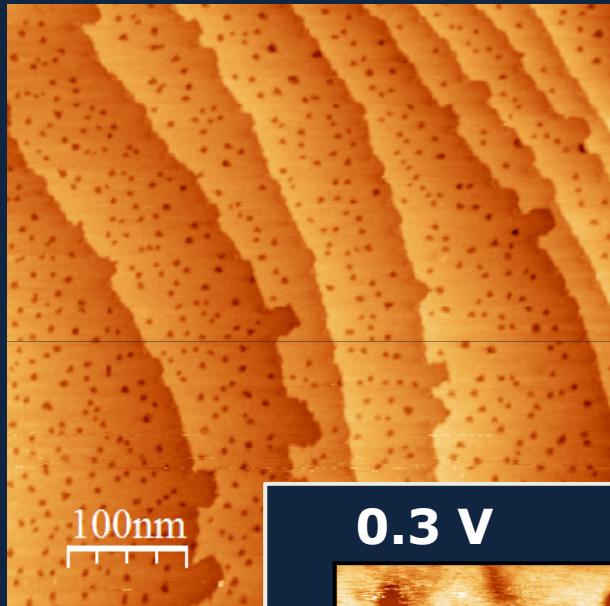


morphology

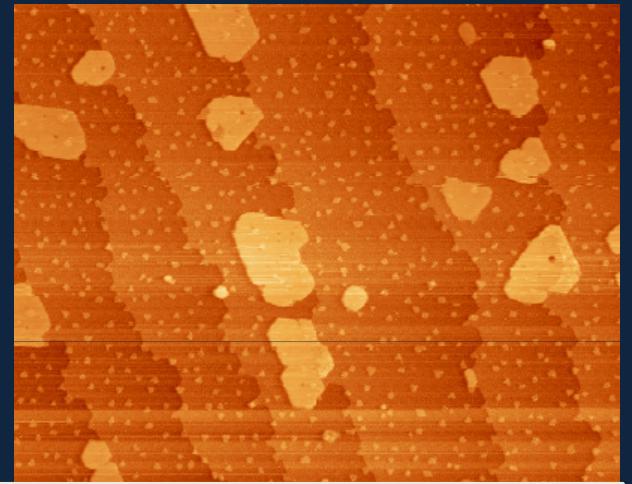
clean Pt(111)



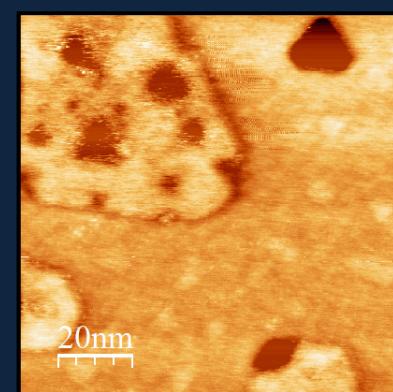
Pt (111)
ann. @ 1040 K O₂



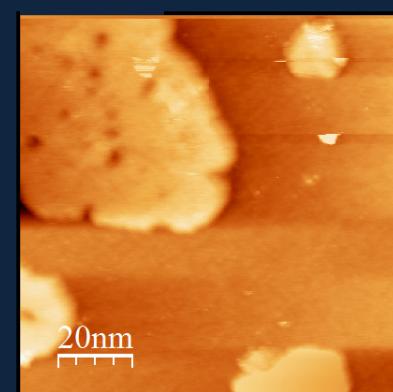
0.2 ML CeO₂
ann. @ 1040 K O₂



0.3 V



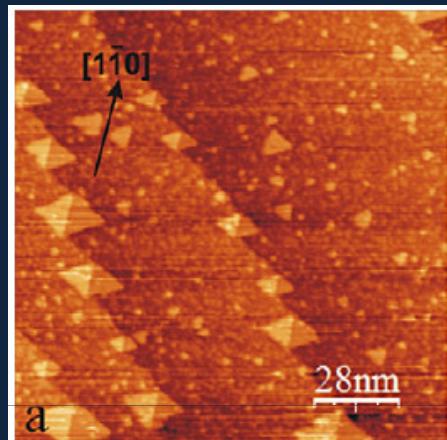
1 V



0.7 ML CeO₂ 0.1nA

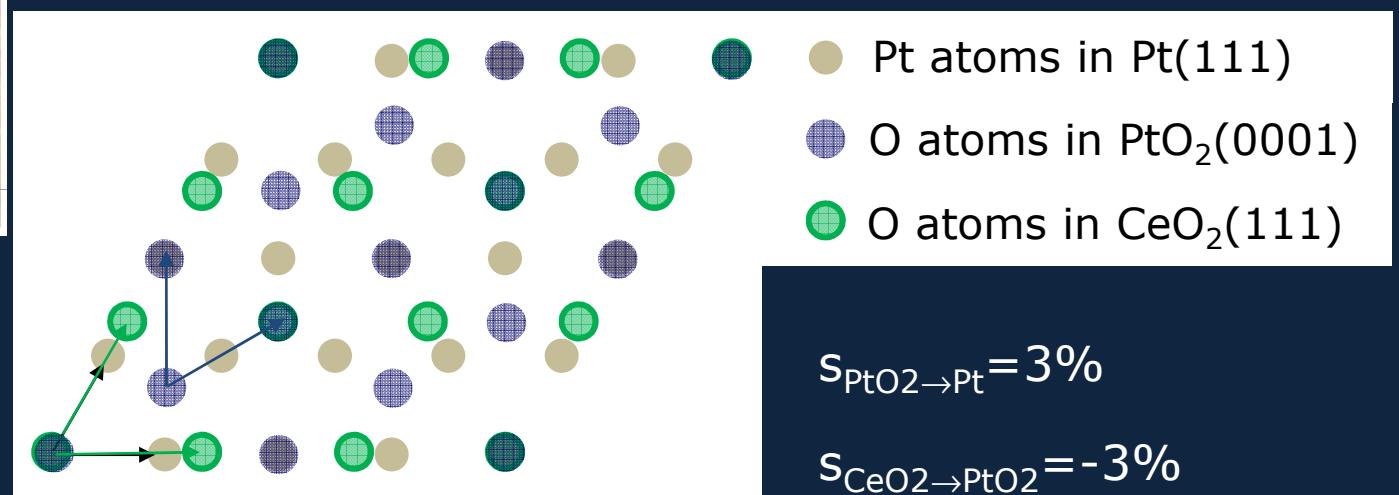
morphology

$\alpha\text{-PtO}_2(0001)$ nanoislands

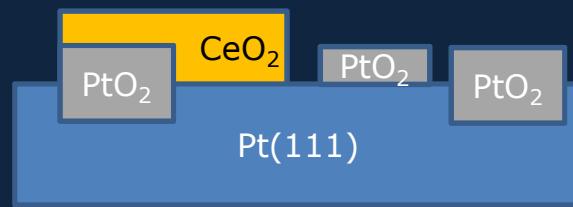


S.A. Karsnikov et al.
Nanotech. 21 (10) 335301

$$a_{\text{Pt}} = 2.78 \text{ \AA}$$
$$a_{\text{PtO}_2} = 3.12 \text{ \AA}$$
$$a_{\text{CeO}_2} = 3.83 \text{ \AA}$$

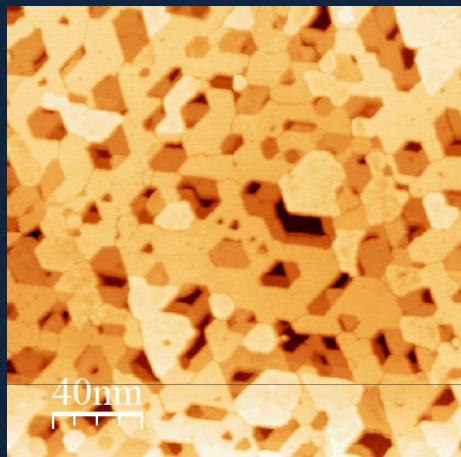


PtO₂ islands may act as a template for the stabilization of CeO₂ in the observed epitaxial orientation

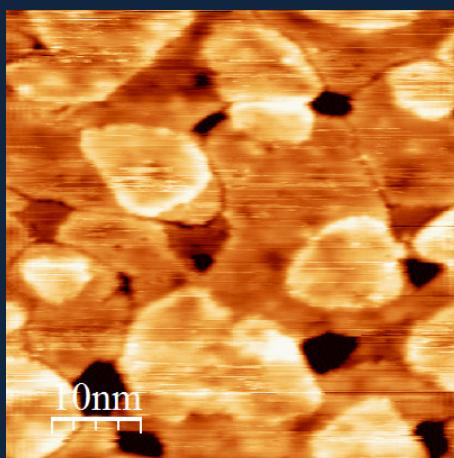
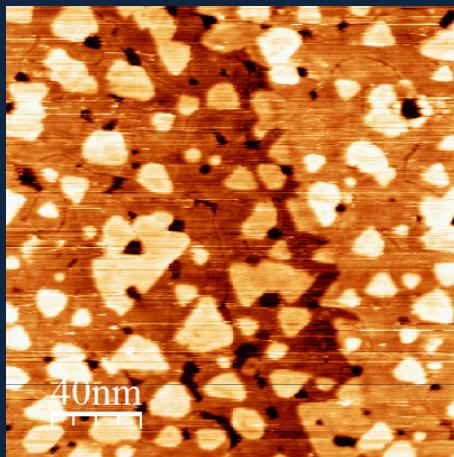


morphology

3.4 ML CeO₂



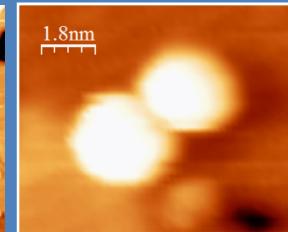
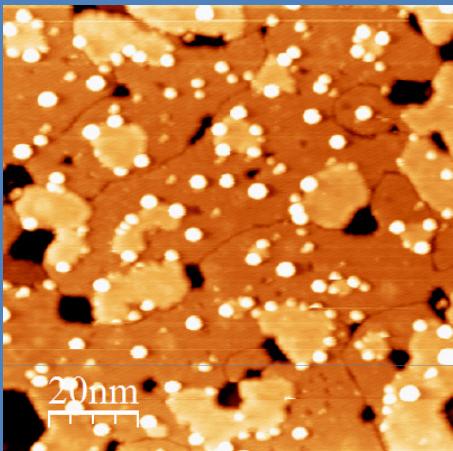
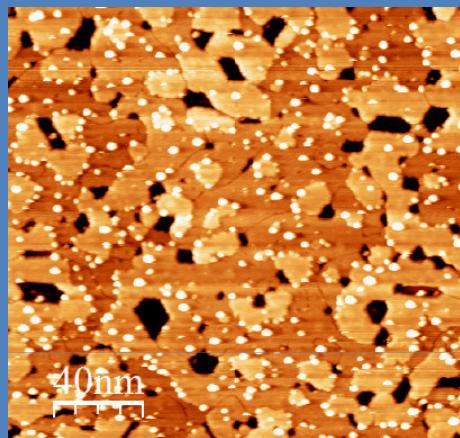
9.3 ML CeO₂



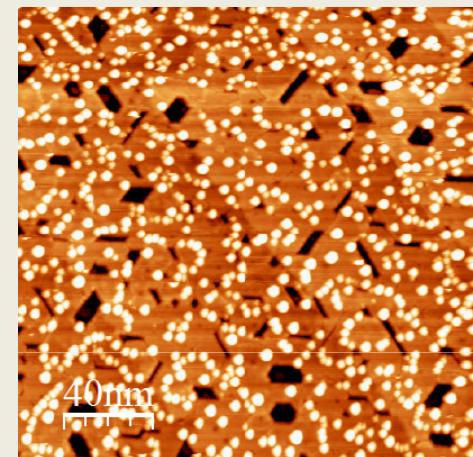
- flat CeO₂ terraces
- straight edges 120°
- linear defects

Ag/CeO₂

0.07 Å Ag / 3 ML CeO₂



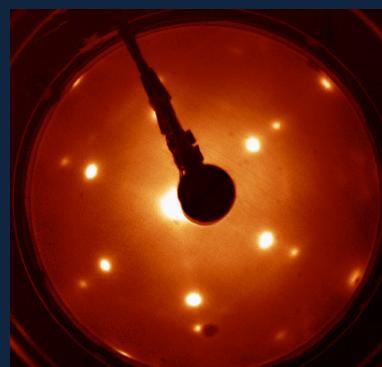
0.2 Å Ag / 3 ML CeO₂



d=0.5-3nm
h=0.5-1 nm

d= 2-5 nm
h=0.5-2 nm

- decoration of CeO₂-CeO₂ steps
 - hexagonal shape → (111) orientation
- epitaxy



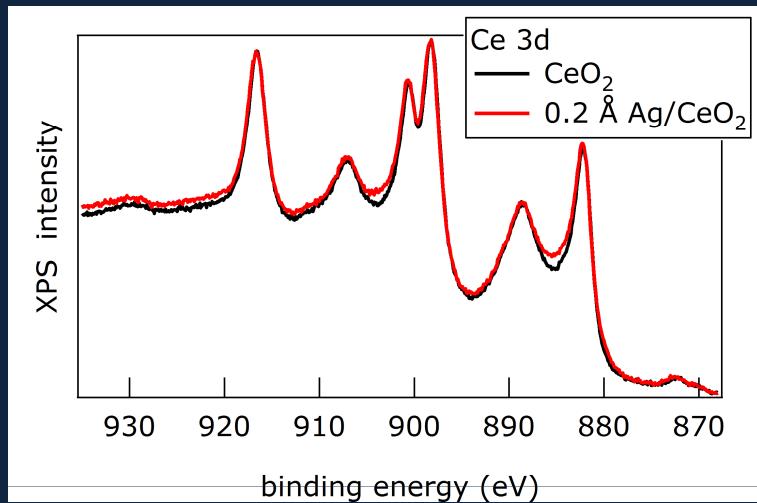
Ag film on CeO₂

$$a_{\text{CeO}_2} = 3.826 \text{ \AA}$$

$$a_{\text{Ag}} = 2.892 \text{ \AA}$$

m=32%

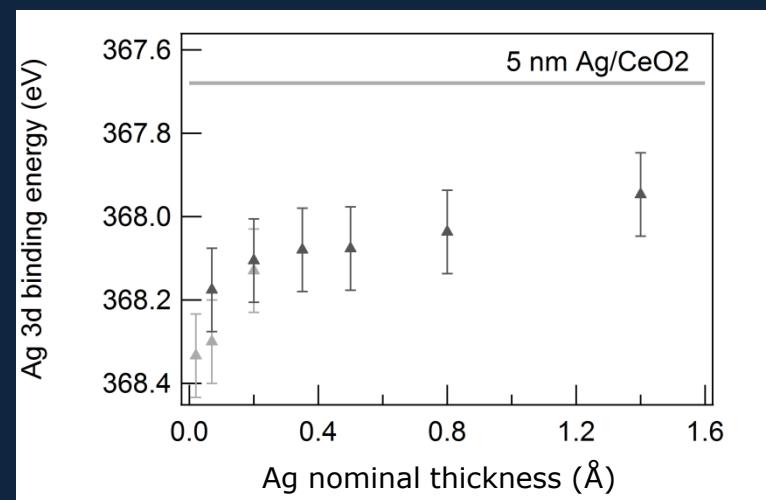
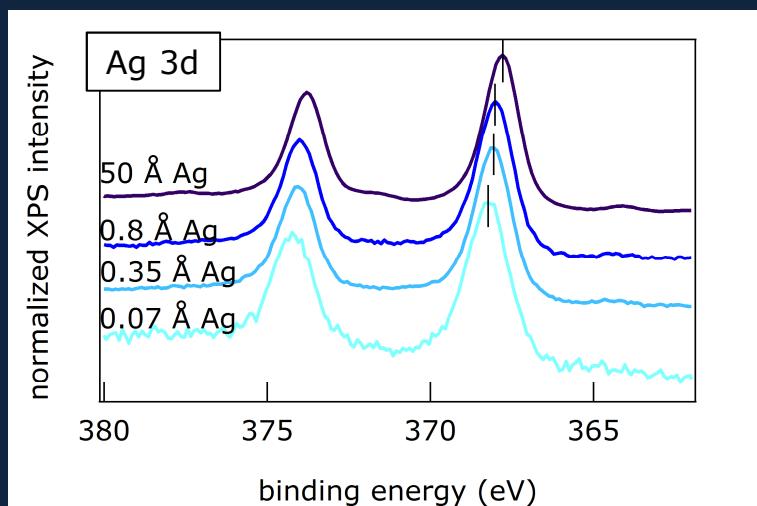
Ag/CeO₂



ceria reduction

higher Ag 3d BE

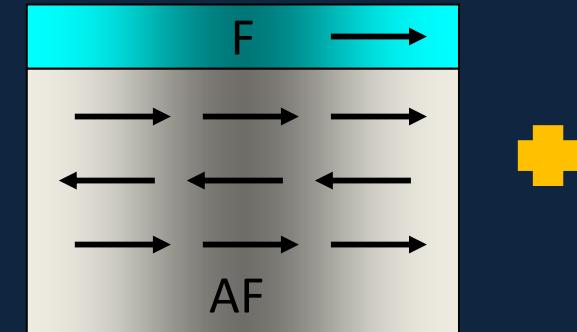
oxidation, dimensionality, charge transfer



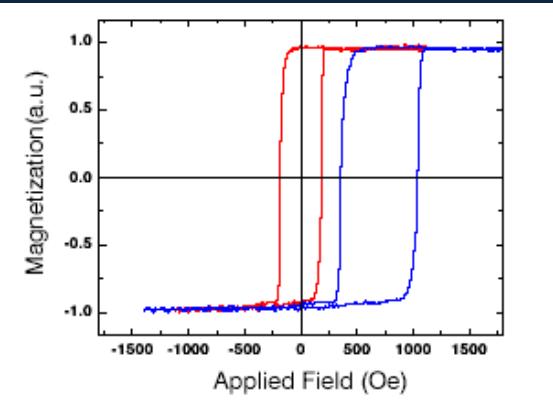
Fe/NiO

motivation

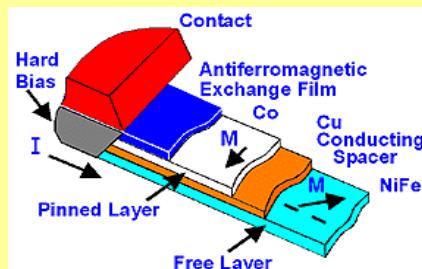
F/AF interface – exchange bias



heating up to T_N
+
cooling in H



pinning of the magnetization of one of the FM layers in magnetoresistive devices



exchange bias

extra source of anisotropy to shift the SPM limit in ultrahigh density magnetic memories

V. Skumryev et al., Nature 423 (2003) 850.

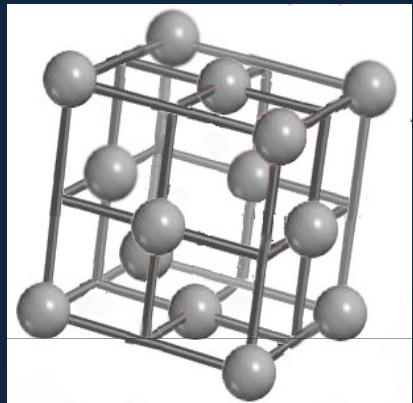
- no complete and quantitative physical model of exchange bias
- strong dependence on the structure of the interfaces



study of atomic-scale characterized systems

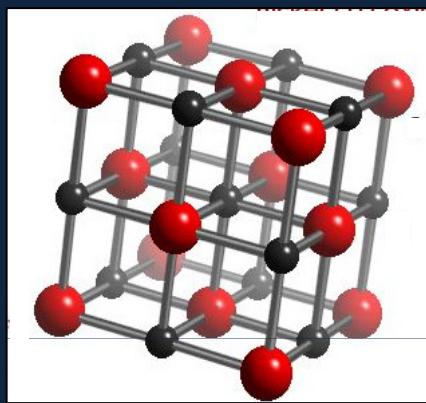
structure

Ag



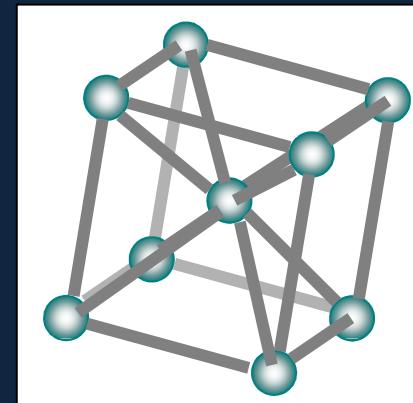
$$a_{\text{Ag}} = 4.086 \text{ \AA}$$

NiO



$$a_{\text{NiO}} = 4.176 \text{ \AA}$$

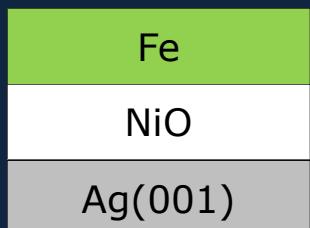
Fe



$$a_{\text{Fe}} = 2.866 \text{ \AA}$$
$$d_{\text{Fe}} = 4.053 \text{ \AA}$$

$$m_{\text{NiO-Ag}} \sim 2\%$$

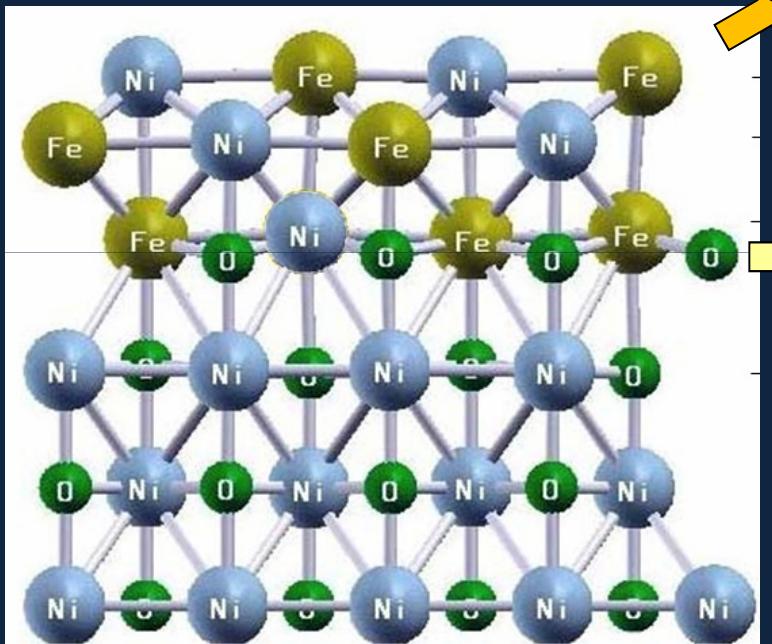
$$m_{\text{Fe-NiO}} \sim 3\%$$



epitaxial system

$$\text{NiO } T_N = 520 \text{ K} \gg RT$$

previous studies



bct Fe-Ni alloy formation (3 ML)

P. Luches et al., Surf. Sci. 532 (2003) 409.
S. Benedetti et al., Surf. Sci. 572 (2005) L348.

planar FeO-like phase

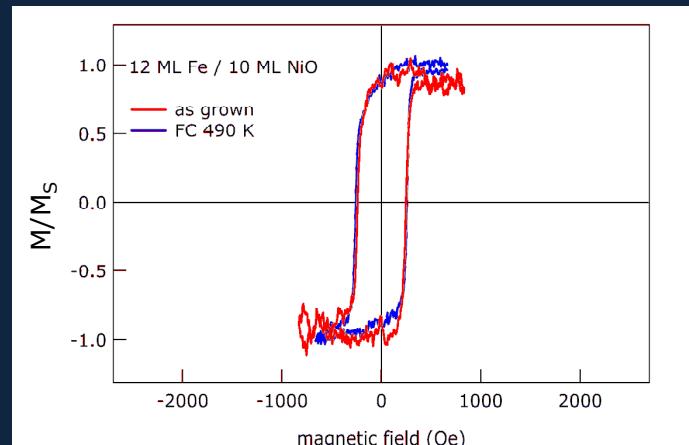
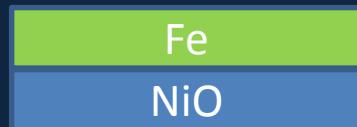
P. Luches et al. , Phys. Rev. Lett. 96 (2006)
106106.

NiO reduction+ Fe oxidation

T.J. Regan et al., Phys. Rev. B 64 (2001) 214422.
R. De Masi et al. Surf. Sci. 513 (2002) 523.

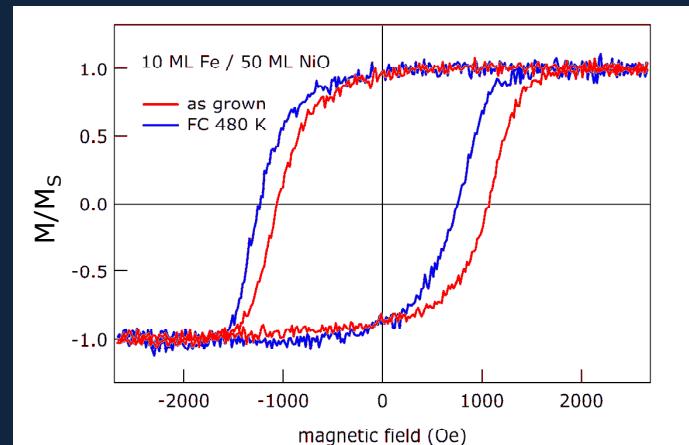
magnetic properties

MOKE



$$H_{EB} = 0 \text{ Oe}$$

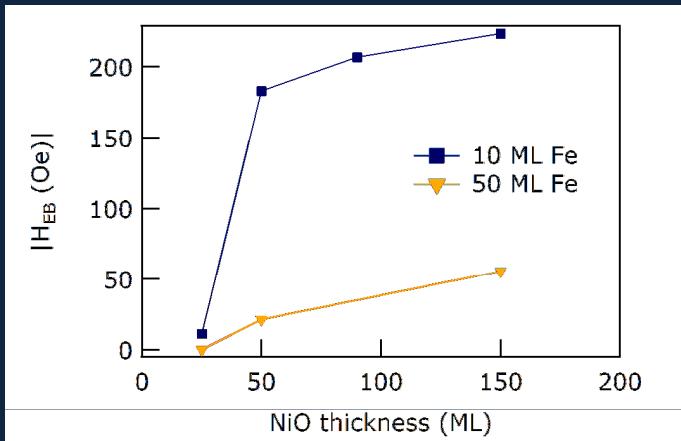
no EB for $t_{\text{NiO}} \leq 25 \text{ ML}$



$$H_{EB} = -220 \text{ Oe}$$

magnetic properties

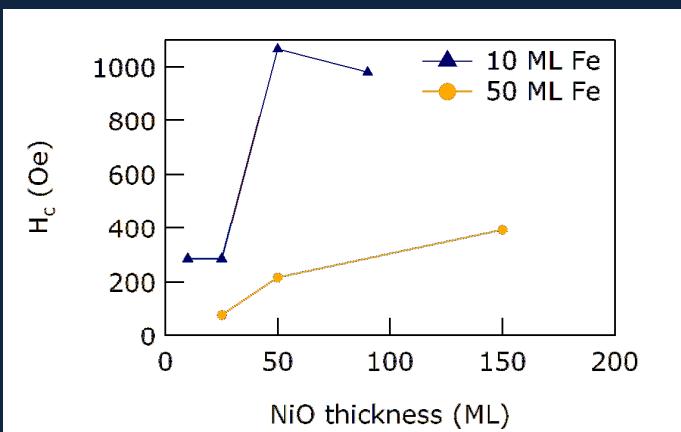
exchange bias



role of the interface

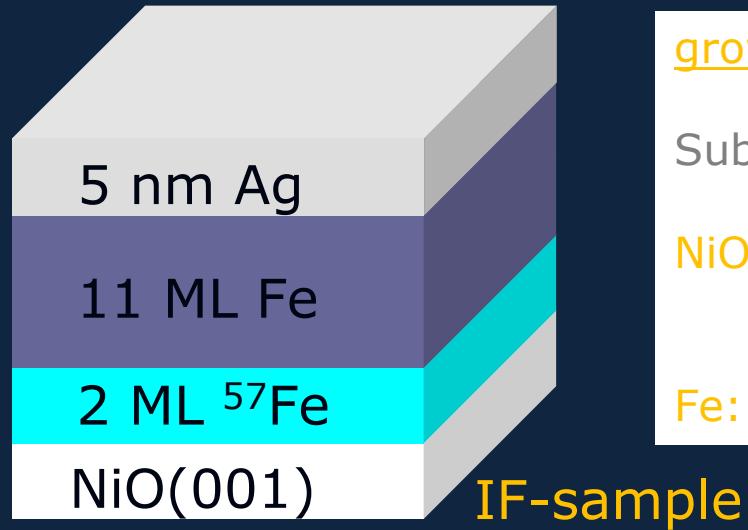
oxidized Fe phase
uncompensated moments in NiO

coercive field



depth resolved magnetic characterization by NRS

experimental



growth conditions

Substrate: Ag(001)

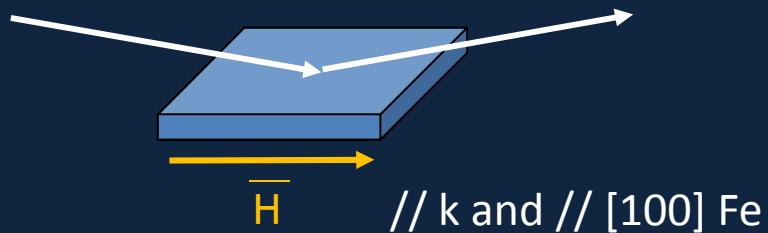
NiO: $R_{\text{Ni}} \sim 1 \text{ \AA/min}$ $P_{\text{O}_2} \sim 1 \times 10^{-7} \text{ torr}$
 $T_{\text{Ag}} = 460 \text{ K}$

Fe: $R_{\text{Fe}} \sim 1 \text{ \AA/min}$ RT



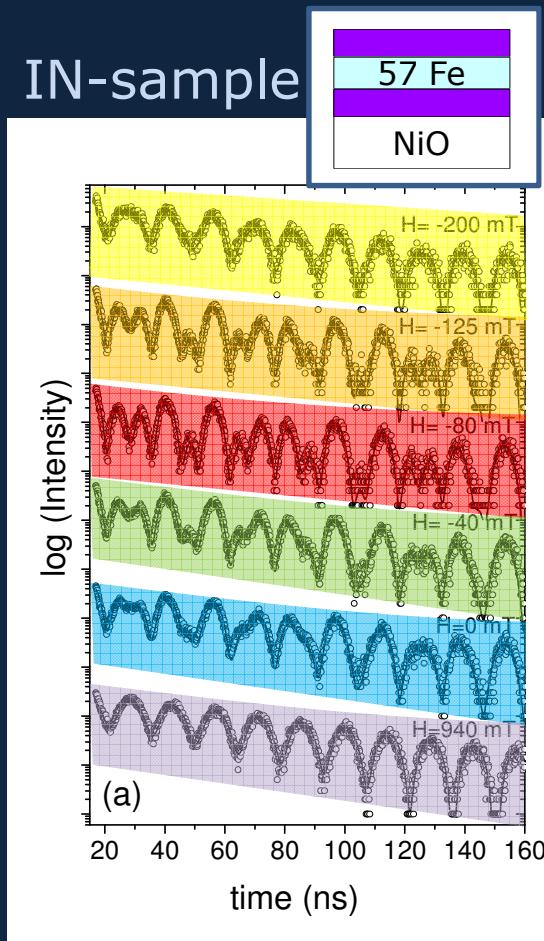
+ NRS measurements
@ ESRF ID18

$\hbar\nu = 14.4 \text{ keV}$ $\Delta t = 176 \text{ ns}$

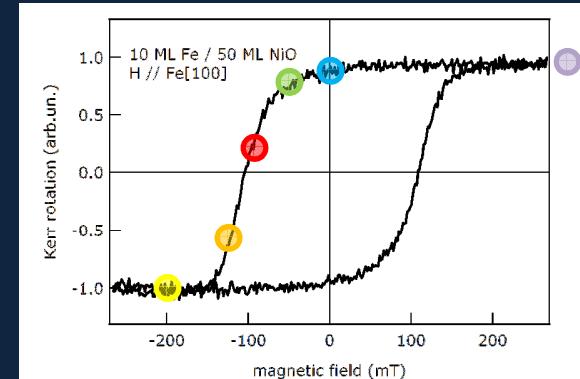
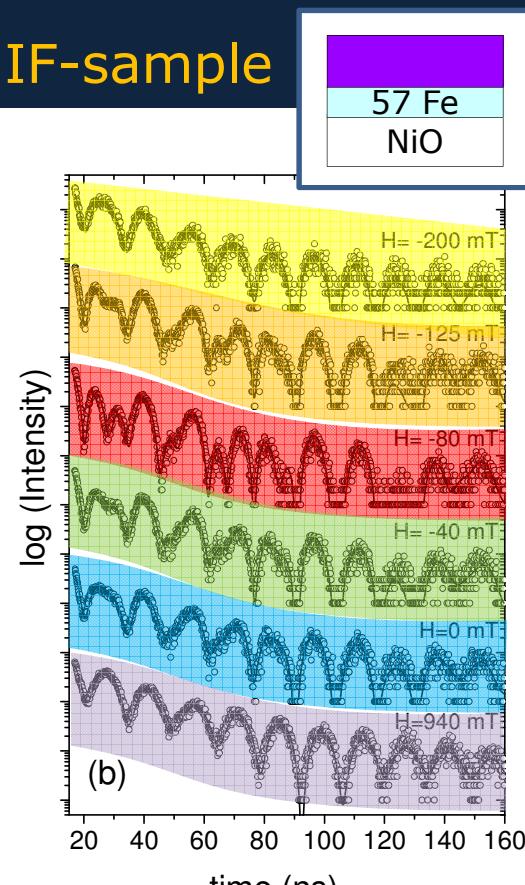


NRS data

IN-sample



IF-sample



fit by NRS package
by C. L'abbe
W. Sturhan, HH 125 (200) 149

Sample	Component #	IS (mm/s)	B_{HF} (T)	$\Delta B_{HF} / B_{HF}$ (%)	RW (%)
IN	1	0 fixed	-33.2 (2)	2	100
IF	1	0 fixed	-33.5 (2)	6 (1)	60 (6)
	2	0.42 (5)	-37.2 (3)	11 (2)	20 (2)
	3	0.42 (5)	+25.3 (5)	90 (5)	20 (2)

metallic

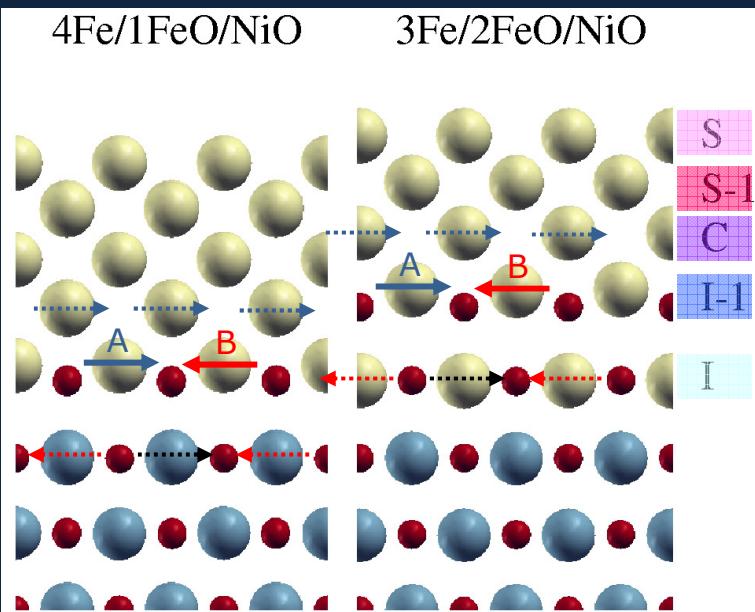
metallic

oxidized

large $|B_{HF}|$

comparison with theory

DFT APW+lo GGA



System	4Fe/1FeO/NiO		3Fe/2FeO/NiO	
	$B_{HF}(T)$	$m(\mu_B)$	$B_{HF}(T)$	$m(\mu_B)$
S	-24,-25	2.9	-22,-22	3.0
S-1	-37,-37	2.4	-37,-33	2.5
C	-32,-28	2.5	-25,-25	2.7
I-1	-31,-30	2.4	-37+14	3.1
I	-37+17	3.1	-35+37	3.5

AFM config. for Fe atoms in FeO

$$B_{hf} = B_C + \cancel{B_{dip}} + \cancel{B_{orb}}$$

$$B_C = B_{core} + B_{val}$$

$$B_{val} = B_{LOC} + B_{NON-LOC}$$

$$|B_A| = |B_{core} + B_{LOC} + 4B_{NN}|$$

$$|B_B| = |B_{core} + B_{LOC} - 4B_{NN}|$$

asymmetry in positive and negative B_{hf}

NRS

Sample	Component #	IS (mm/s)	$B_{HF}(T)$	$\Delta B_{HF}/B_{HF} (\%)$	RW (%)
IF	1	0 fixed	-33.5 (2)	6 (1)	60 (6)
	2	0.42 (5)	-37.2 (3)	11 (2)	20 (2)
	3	0.42 (5)	+25.3 (5)	90 (5)	20 (2)

⇒ antiferromagnetic FeO phase

P. Luches et al., PRB 83 (2011) 094413

summary

CeO₂

- CeO₂(111) films with wide flat terraces can be obtained on Pt(111)
- the Ce³⁺ concentration in the films can be reversibly modified by thermal treatments in UHV or O₂
- Ag nanoparticles reduce ceria and have a higher 3d BE than the bulk

Fe/NiO

- an antiferromagnetic Fe oxide layer is present at the interface
- DFT calculations can be of great help to interpret the NRS data

People

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