Electronic Supplementary Information

Influence of the lattice constant on defects in cerium oxide

Steffen Grieshammer

Helmholtz-Institut Münster (IEK-12), Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany
Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany
JARA-HPC, RWTH Aachen University and Forschungszentrum Jülich GmbH, 52056 Aachen, Germany

Dependence of the lattice constant on U_{eff}

The equilibrium lattice constant a_0 was determined for varying values of U_{eff} for the PBE and PBEsol functional as shown in Fig. S4.

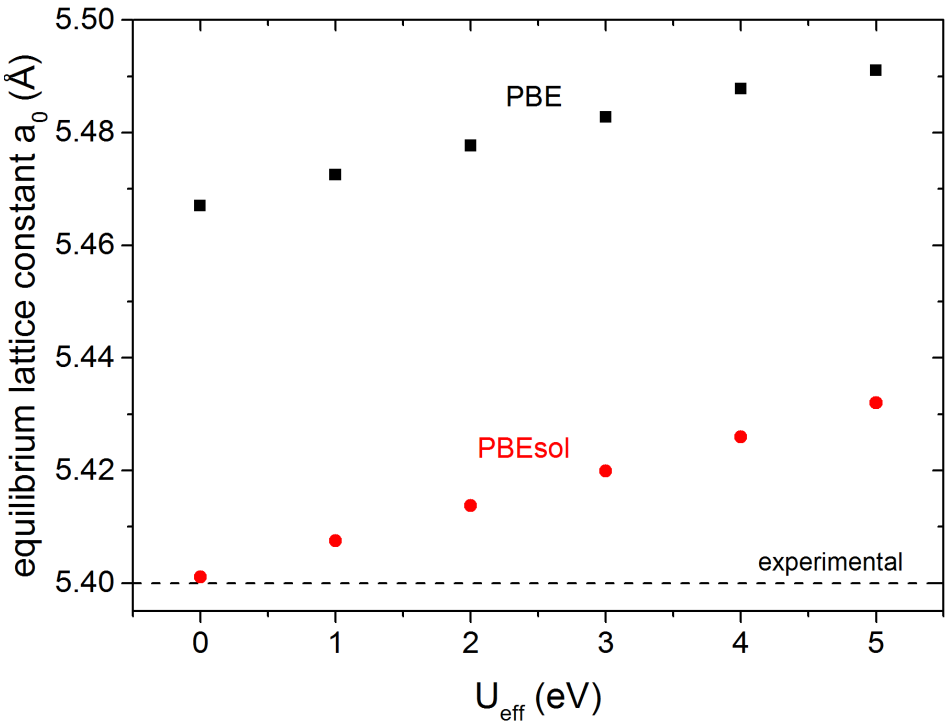

Fig. S1: Dependence of the calculated equilibrium lattice constant on the effective *U*-parameter.

Birch-Murnaghan equation of state fits for defective cells

Supercells with different defects were calculated with the GGA functionals PBE and PBEsol and the hybrid functional HSE06. For the GGA functionals a Hubbard *U*-parameter of U_{eff} = 5 eV was introduced for the 4*f*-orbitals of cerium in the simplified rotational invariant approach. The energy-volume relationship was fitted by a Birch-Murnaghan equation of state:

$$E = E_0 + \frac{9V_0B}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^3 B' + \left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]^2 \left[6 - 4\left(\frac{V_0}{V}\right)^{2/3}\right]\right\}$$

The results for the cells, calculated with the three functionals, are given in the following.

PBE

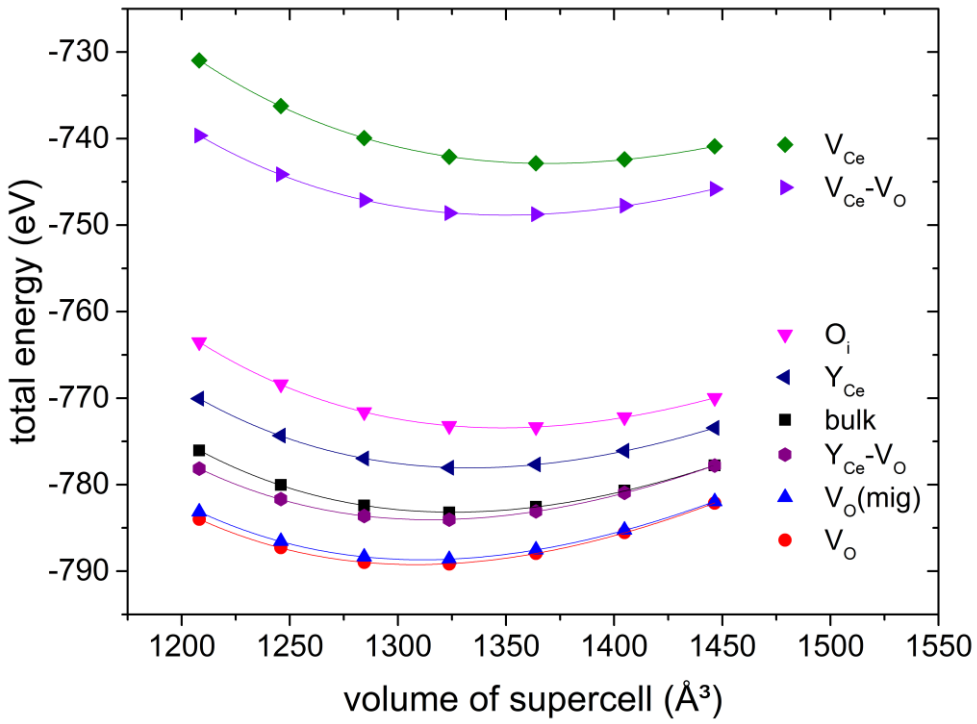

Fig. S2: Energy-volume relationship for supercells calculated with PBE.

Table S1: Parameters obtained from the equation of state fit for the supercells calculated with PBE.

cell	E_0 (eV)	V_0 (Å^3)	B (eV/ Å^3)	B' (-)
bulk	-783.18 ± 0.02	1325.51 ± 0.51	1.16 ± 0.01	4.65 ± 0.34
$V_O^{\cdot\cdot}$	-789.24 ± 0.02	1308.22 ± 0.49	1.18 ± 0.01	4.70 ± 0.34
$V_O^{\cdot\cdot}$(mig)	-788.68 ± 0.02	1311.39 ± 0.51	1.17 ± 0.01	4.72 ± 0.35
O_i''	-773.43 ± 0.02	1348.26 ± 0.46	1.11 ± 0.01	4.67 ± 0.35
V_{Ce}''''	-742.87 ± 0.02	1369.02 ± 0.40	1.00 ± 0.01	4.57 ± 0.35
Y_{Ce}'	-778.05 ± 0.02	1333.58 ± 0.50	1.13 ± 0.01	4.65 ± 0.35
$V_{Ce}'''' - V_O^{\cdot\cdot}$	-748.83 ± 0.03	1349.66 ± 0.55	1.00 ± 0.01	4.85 ± 0.43
$Y_{Ce}' - V_O^{\cdot\cdot}$	-784.05 ± 0.02	1315.39 ± 0.52	1.15 ± 0.01	4.73 ± 0.35

PBEsol

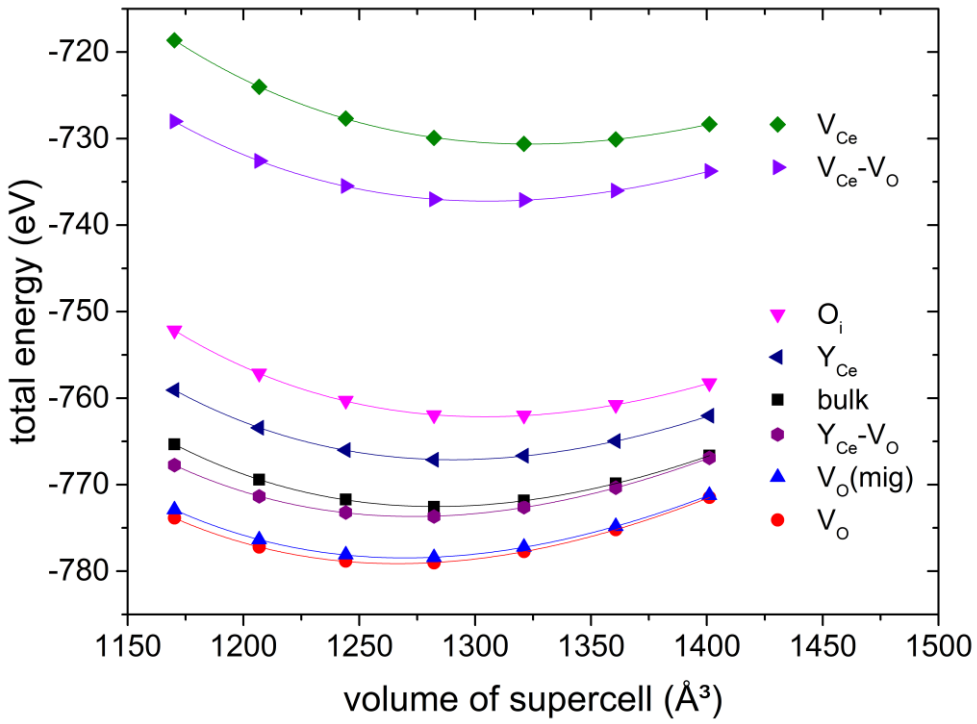

Fig. S3: Energy-volume relationship for supercells calculated with PBEsol.

Table S2: Parameters obtained from the equation of state fit for the supercells calculated with PBEsol.

cell	E_0 (eV)	V_0 (Å^3)	B (eV/ Å^3)	B' (-)
bulk	-772.53 ± 0.02	1282.98 ± 0.46	1.25 ± 0.01	3.91 ± 0.32
$V_O^{\cdot\cdot}$	-779.13 ± 0.02	1266.52 ± 0.45	1.26 ± 0.01	3.94 ± 0.33
$V_O^{\cdot\cdot}$(mig)	-778.46 ± 0.02	1269.60 ± 0.46	1.25 ± 0.01	3.94 ± 0.33
O_i''	-762.15 ± 0.02	1304.21 ± 0.42	1.22 ± 0.01	3.92 ± 0.32
V_{Ce}''''	-730.63 ± 0.02	1323.68 ± 0.37	1.11 ± 0.01	3.80 ± 0.33
Y_{Ce}'	-767.11 ± 0.02	1290.53 ± 0.45	1.22 ± 0.01	3.90 ± 0.32
$V_{Ce}'''' - V_O^{\cdot\cdot}$	-737.22 ± 0.02	1305.26 ± 0.44	1.10 ± 0.01	3.86 ± 0.34
$Y_{Ce}' - V_O^{\cdot\cdot}$	-773.68 ± 0.02	1273.31 ± 0.46	1.24 ± 0.01	3.95 ± 0.32

HSE06

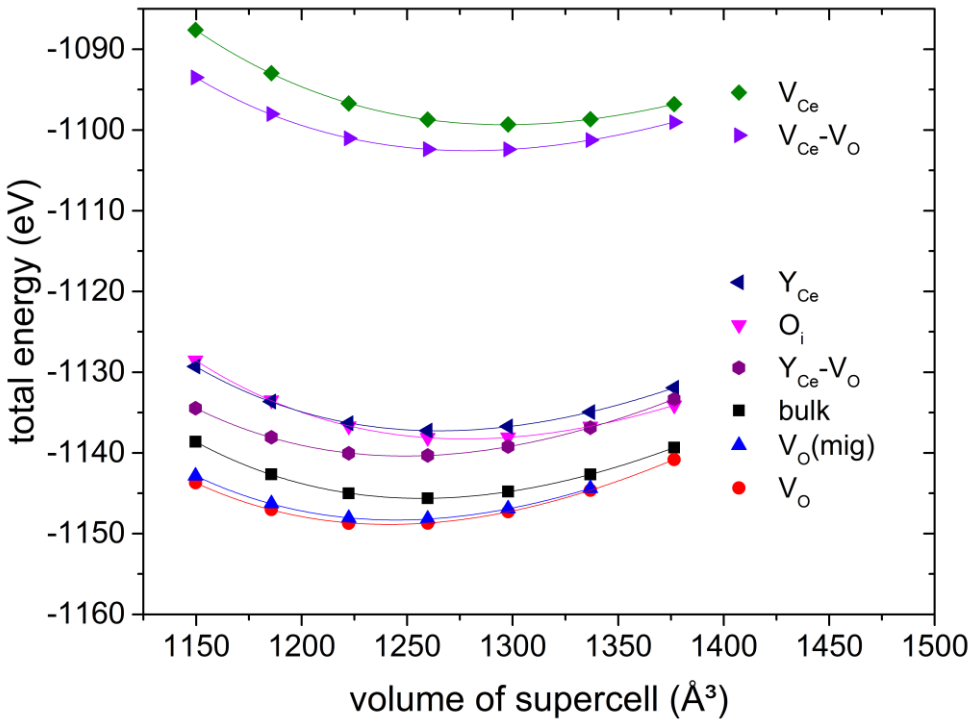

Fig. S4: Energy-volume relationship for supercells calculated with HSE06.

Table S3: Parameters obtained from the equation of state fit for the supercells calculated with HSE06.

cell	E_0 (eV)	V_0 (Å^3)	B (eV/ Å^3)	B' (-)
bulk	-1145.62 ± 0.02	1256.91 ± 0.53	1.30 ± 0.01	4.49 ± 0.37
$V_O^{\cdot\cdot}$	-1148.86 ± 0.02	1241.45 ± 0.50	1.32 ± 0.01	4.54 ± 0.37
$V_O^{\cdot\cdot}(mig)$	-1148.30 ± 0.03	1244.56 ± 0.82	1.31 ± 0.02	4.53 ± 0.82
O_i''	-1138.27 ± 0.03	1277.64 ± 0.50	1.25 ± 0.01	4.52 ± 0.38
V_{Ce}''''	-1099.35 ± 0.03	1296.35 ± 0.44	1.14 ± 0.02	4.39 ± 0.39
Y_{Ce}'	-1137.25 ± 0.02	1265.12 ± 0.52	1.27 ± 0.01	4.54 ± 0.37
$V_{Ce}'''' - V_O^{\cdot\cdot}$	-1102.56 ± 0.03	1279.58 ± 0.58	1.11 ± 0.01	4.97 ± 0.46
$Y_{Ce}' - V_O^{\cdot\cdot}$	-1140.38 ± 0.02	1248.84 ± 0.52	1.29 ± 0.01	4.55 ± 0.38

Defect formation and interaction with U_{eff}=0

For comparison, energies of formation and defect interaction were calculated for the PBE functional without *U*-parameter.

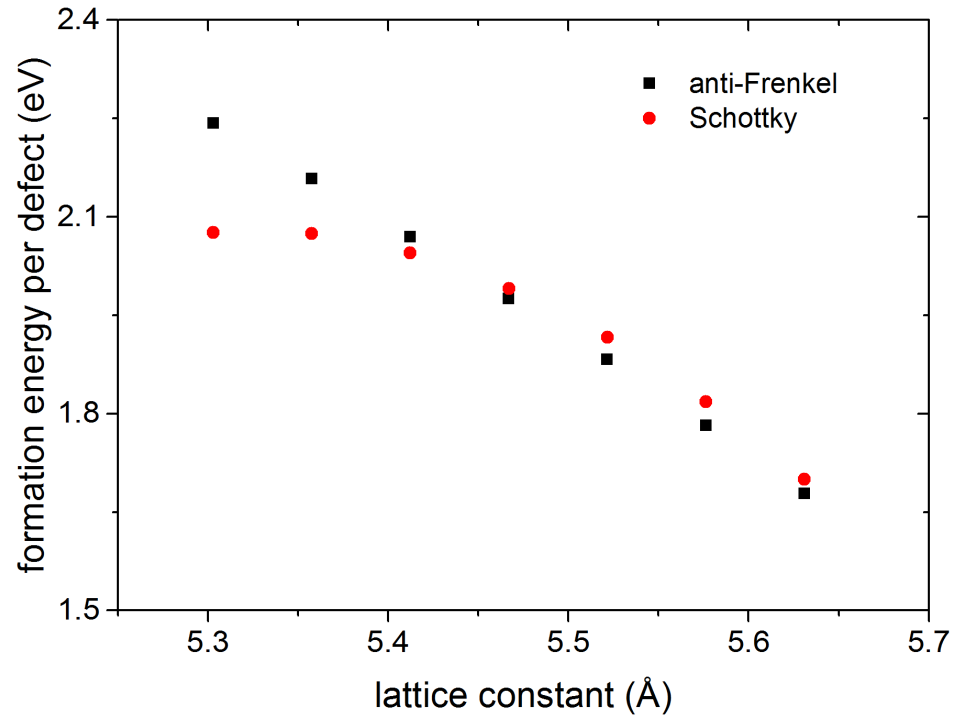

Fig. S5: Energy of defect formation for anti-Frenkel and Schottky disorder per defect for the PBE functional with U_{eff}=0.

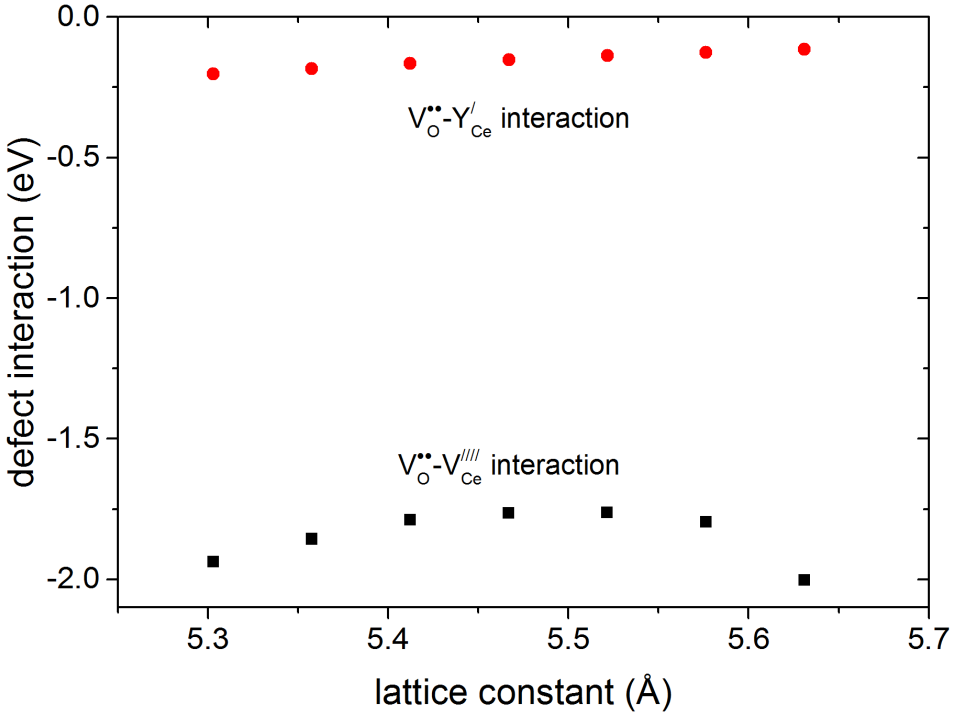

Fig. S6: Interaction energy between Y-dopant and oxygen vacancy as well as cerium vacancy and oxygen vacancy for the PBE functional with U_{eff}=0.

Relation between lattice constant and defect energy

The calculated defect energies as function of the lattice constant where fitted by linear or parabolic functions depending on the curve form. Results are given in

Table 4: Relation between defect energy ΔE and lattice constant x fitted by the expression $\Delta E = a + b \cdot x$.

	PBE		PBEsol		HSE06	
	a (eV)	b (eV/Å)	a (eV)	b (eV/Å)	a (eV)	b (eV/Å)
ΔE_{aF}	13.10	-2.00	13.01	-2.00	14.62	-2.29
$\Delta E_{\mathrm{Y-VO}}$	-4.99	0.85	-5.03	0.86	-5.64	1.00
ΔE_{mig}	11.81	-2.06	12.33	-2.16	12.96	-2.31

Table 5: Relation between defect energy ΔE and lattice constant x fitted by the expression $\Delta E = a + b \cdot x + c \cdot x^2$.

	PBE			PBEsol			HSE06		
	a (eV)	b (eV/Å)	c (eV/Å²)	a (eV)	b (eV/Å)	c (eV/Å²)	a (eV)	b (eV/Å)	c (eV/Å²)
ΔE_{Sch}	-110.53	42.93	-4.07	-118.17	46.31	-4.43	-112.34	44.72	-4.35
$\Delta E_{\mathrm{VCe-VO}}$	-152.45	54.10	-4.87	-143.97	50.71	-4.53	-227.99	81.65	-7.38