

## Supporting Information

# Charge Localization Increases Chemical Expansion in Cerium-based Oxides

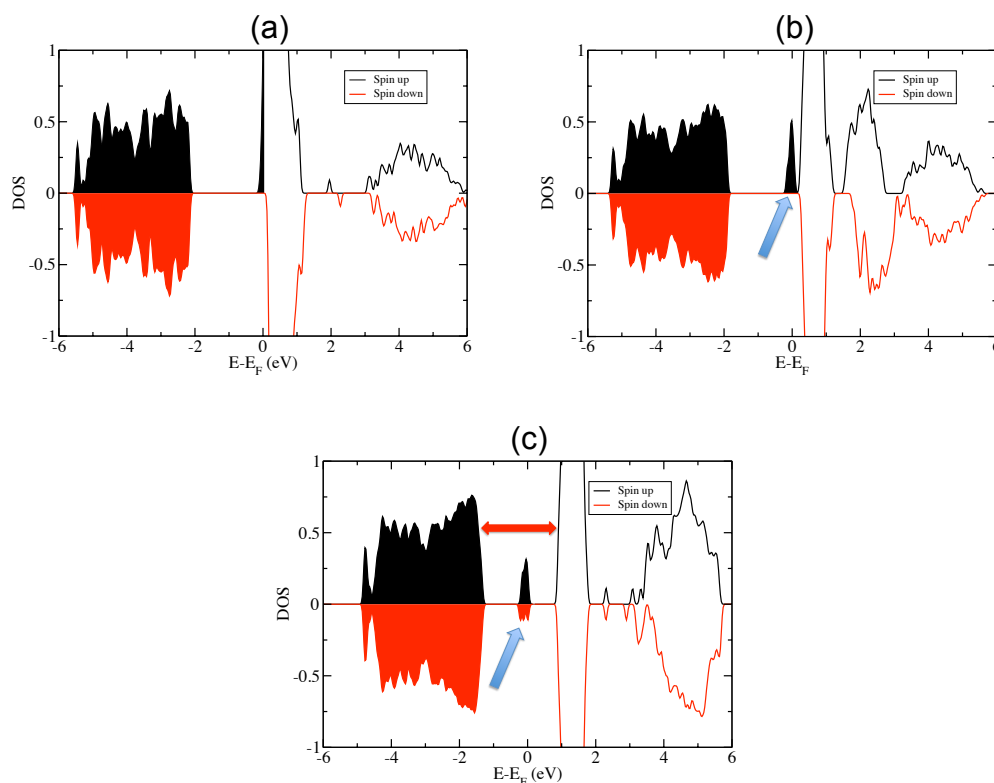
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**Figure S 1:** Total Density of States (DOS) for  $U = 0, 3$  and  $5$  eV in (a), (b) and (c), respectively. Occupied states are indicated by shaded areas and energies are plotted with respect to the Fermi level. Simple DFT, (a), gives rise to a density of states with no energy gap between the valence and the conduction band, with the Ce 4f states crossing the Fermi level, i.e. a metallic solution. When the  $U$  term is added, the appearance of a new Ce 4f state occurs (see blue arrows in (b) and (c)) is observed. For  $U = 3$  eV, these occupied states are not fully separated from the unoccupied ones. This is achieved for  $U = 5$  eV, where we also observed the opening of a band gap (from the valence band to the unoccupied Ce 4f band) of 2.1 eV, as indicated by the red arrow in (c).

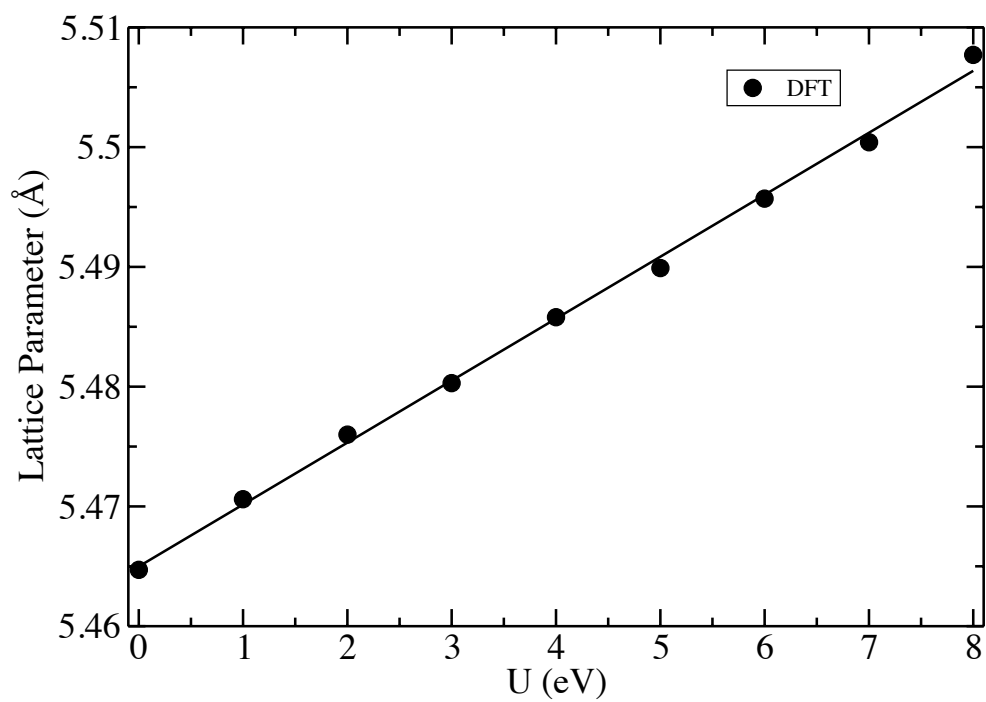


Figure S 2: Lattice parameter of CeO<sub>2</sub> vs Hubbard term, U. The points are from a DFT calculation whereas the straight line is a guide to the eye.

Table I: Ionic projected spin density of the  $\text{Ce}^{3+}$  cation shown in Figure 1 for different  $U$  values. For  $U > 5.0$  eV the spin density reaches a value of approximately 1, thus confirming the localization of the 4f electrons.

U (eV)	$\text{Ce}^{3+}$ projected spin density
0	0.048
1	0.069
2	0.025
3	0.655
4	0.893
5	0.941
6	0.955
7	0.965
8	0.972

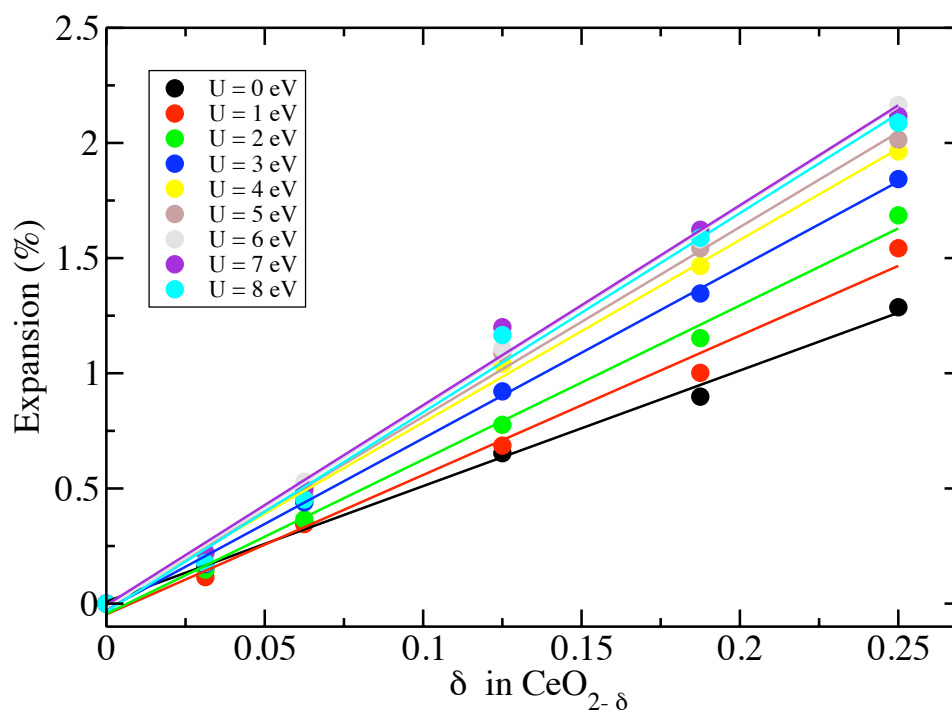


Figure S 3: : Lattice parameter expansion (%) vs  $\delta$  for  $\text{CeO}_{2-\delta}$  for different  $U$  values. Solid lines are linear fits.

Table II: Calculated ionic radii for different  $U$  values.

$U$ (eV)	$\text{Ce}^{3+}$ ionic radius ( $\text{\AA}$ )
0	1.082
1	1.093
2	1.101
3	1.110
4	1.116
5	1.119
6	1.125
7	1.125
8	1.124

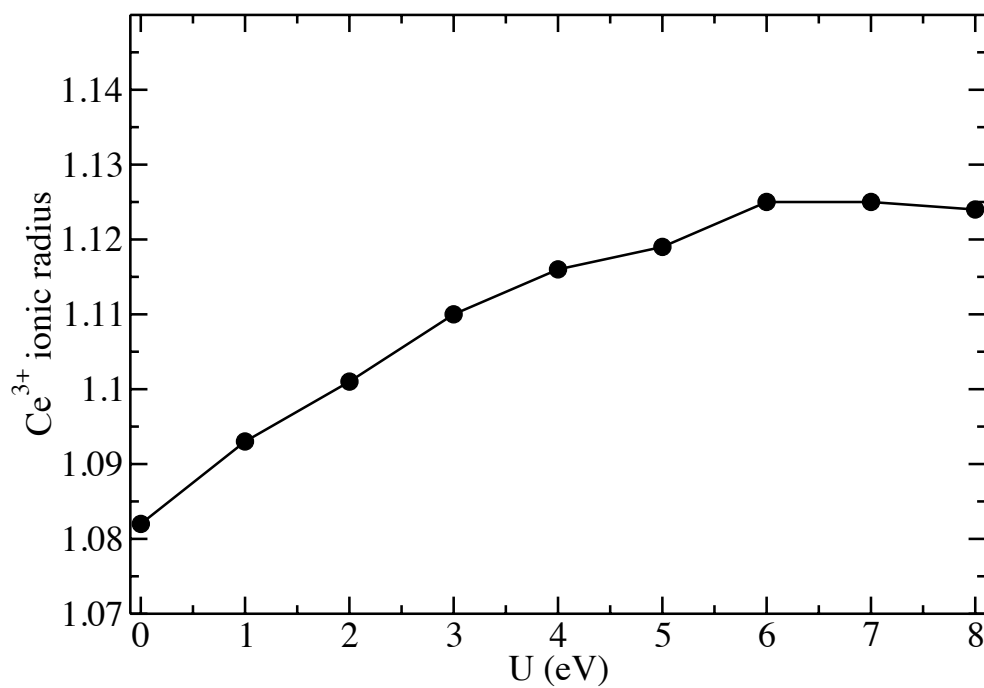


Figure S 4: Calculated ionic radii for different  $U$  values.