# Supporting Information to

## *Combined DFT and experimental study of the dispersion and interaction of copper species in Ni-CeO$_2$ nanosized solid solutions*

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# 1 - On the Energetic Stability of the Solid Solutions

In order to probe the corresponding stability of the NiCeO$_\delta$ and Cu-modified NiCeO$_\delta$ solid solutions as a function of the Hubbard (+U) corrections, we performed an extensive set of DFT+U calculations in which the values of the +U parameters were systematically varied. Table S1 indicate the obtained formation energies of the NiCeO$_\delta$ solid solutions as a function of the +U term. It is interesting to note that the formation energies are relatively independent of the choice of the +U parameter, being in good agreement with the conclusions drowned by Wang and co-workers [Supplementary Reference (SR) 1]. In Figure S1 we have plotted the values of the formation energies as a function of +U, extending the calculations to some higher values (5.0, 5.6, 6.0 and 6.6 eV).

**Table S1** – Energy of formation (eV) of the NiCeO$_\delta$ Solid Solutions as a Function of the +U Term

| Ni (%) | U = 0 | U = 0.6 | U = 1.6 | U = 2.6 | U = 3.6 | **U = 4.6** | U = 5.0 | U=5.6 | U=6.0 | U = 6.6 |
|--------|-------|---------|---------|---------|---------|-------------|---------|-------|-------|---------|
| 3.12 | 2.63 | 2.62 | 2.84 | 2.61 | 2.85 | **2.75** | 2.89 | 3.06 | 3.08 | 3.17 |
| 6.25 | 5.86 | 5.88 | 6.09 | 5.86 | 6.08 | **5.98** | 6.01 | 6.26 | 6.27 | 6.35 |
| 9.37 | 9.62 | 9.69 | 9.93 | 9.72 | 9.97 | **9.92** | 10.04 | 10.23 | 10.26 | 10.37 |
| 12.50 | 10.15 | 10.24 | 10.42 | 10.16 | 10.36 | **10.27** | 10.36 | 10.51 | 10.52 | 10.59 |
| 15.62 | 13.37 | 13.50 | 13.68 | 13.43 | 13.63 | **13.57** | 13.63 | 13.79 | 13.79 | 13.87 |
| 18.75 | 16.39 | 16.58 | 16.78 | 16.55 | 16.99 | **16.73** | 16.78 | 16.94 | 16.94 | 17.02 |
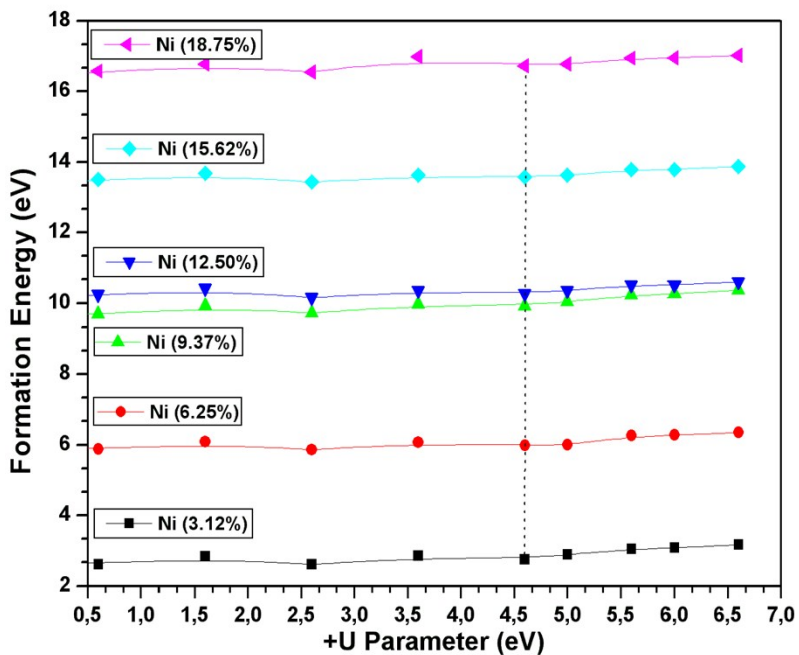
**Figure S1** – Formation energies of the NiCeO$_\delta$ solid solutions as a function of the +U parameter.

It can be seen that the formation energies are nearly linear from U = 0.0 eV until U = 4.6 eV and after that a slight increase is observed. Qualitatively, our findings agrees well with the literature regarding DFT+U calculations on ceria-based systems, which shows that the choice of the +U parameter for Ce usually lies in between 4-6 eV [SR 2- SR 8]. It has been demonstrated that when cerium oxide surfaces are doped with late transition metals the value of +U on Ce (4f) states has a small effect over the energetics of reduction and adsorptions mainly because those dopants, instead of the cerium atoms, turn out to be the reduction centers where charge tends to concentrate [SR 9]. Fig. S2 illustrates how the formation energies of the NiCeO$_\delta$ solid solutions change with the increasing amount of Ni. It can be seen that the curves are similar in shape to those of Fig. 5 (see the main article), varying only slightly with the choice of the +U values.
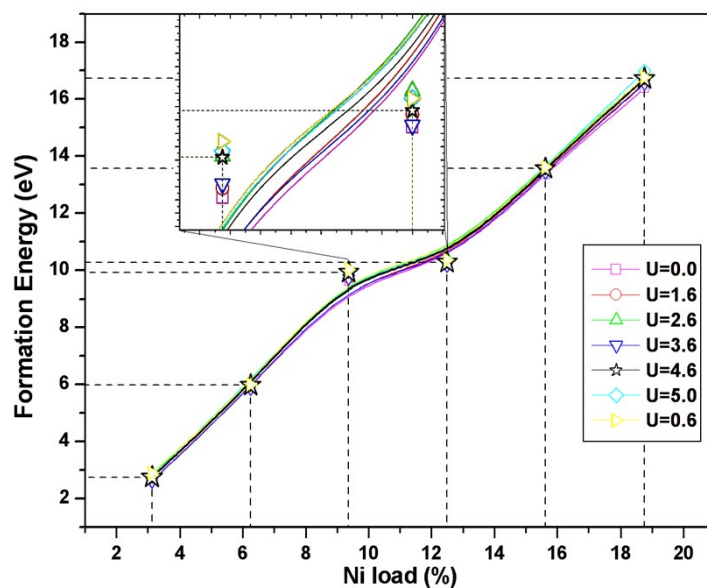
**Figure S2** – Plot of the formation energies of the $NiCeO_\delta$ solid solutions as a function of the amount of Ni dopants. The inset is a magnification of the region between Ni loadings of 9.37% and 12.5% which aims at facilitate the identification of the colors. The dashed lines show the formation energies regarding +U = 4.6 eV (see the main article)

Overall, the same conclusions can be drawn regarding the Cu modified $NiCeO_\delta$ solid solutions. As seen in Fig. S3 and Table 2 (due to the reasons pointed out previously, we limited the theoretical calculations related to the Cu-$NiCeO_\delta$ systems to values of +U ranging from 0.0 eV to 4.6 eV mainly because higher values does not introduce significant changes in the energies), despite the formation energies of the systems "Ni(6.25%)+Cu(3.12%)" and "Cu(6.25%)" present a slight oscillation (mainly when +U values are 1.6 eV and 3.6 eV), there were only a small variation of the values by changing the +U parameters. Notwithstanding, it is possible to conclude that the formation energy of the systems depend only in a small extent of the +U parameter.
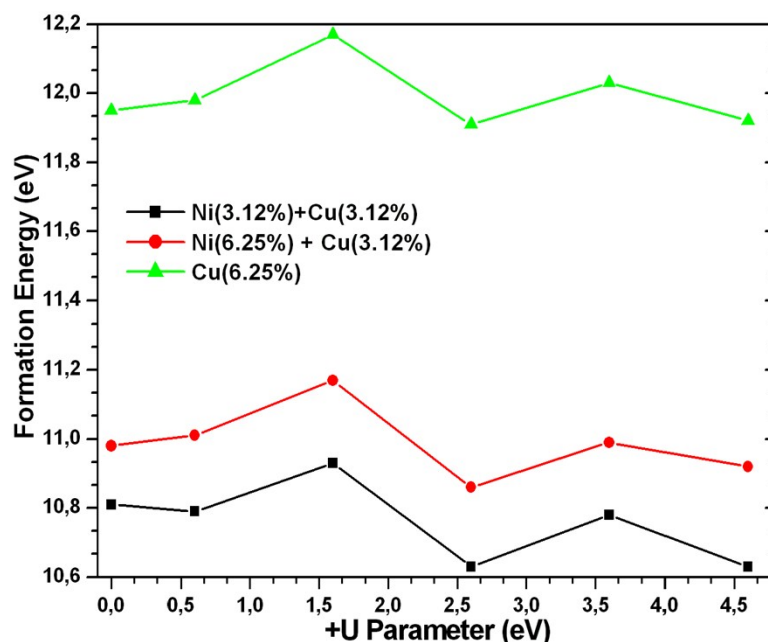
**Figure S3** – Formation energies of the Cu-modified $NiCeO_{\delta}$ (**Cu**-$NiCeO_{\delta}$) solid solutions as a function of +U values.

**Table 2** – Cu-$NiCeO_{\delta}$ Solid Solution Formation Energies (eV) as a Function of the +U term

|  | U = 0 | U = 0.6 | U = 1.6 | U = 2.6 | U = 3.6 | **U = 4.6** |
|---|---|---|---|---|---|---|
| Ni(3.12%) + Cu(3.12%) | 7.93 | 7.99 | 7.95 | 7.91 | 7.87 | **7.85** |
| Ni(6.25%) + Cu(3.12%) | 10.98 | 11.01 | 11.17 | 10.86 | 10.99 | **10.92** |
| Cu(6.25%) | 11.95 | 11.98 | 12.17 | 11.91 | 12.03 | **12.05** |

## 2 - Electronic Structure

As the presence of dopants can largely affect the properties of ceria, it is also important to examine in more detail the electronic structure of the solid solutions. It has been suggested that that the value of the +U parameter has only a small influence over the electronic properties of ceria and its variation produces qualitatively the same electronic distribution [SR 10] (although electron localization effects depend on the choice of the +U parameter, as will

be discussed in the following). Here we investigate the electronic density of states of the doped ceria systems by considering the value of +U = 4.6 eV. Accordingly, the spin polarized projected density of states (PDOS) for the Ce 4f, Ni 3d, Cu 3d and O2p states of the Ce, Ni, Cu and O atoms in the supercells were calculated. The density of states was plotted considering the energy lying in between -5 eV and 3 eV. The Fermi level was located at zero (*i.e.* $E-E_F = 0$), being represented by a vertical dashed line.
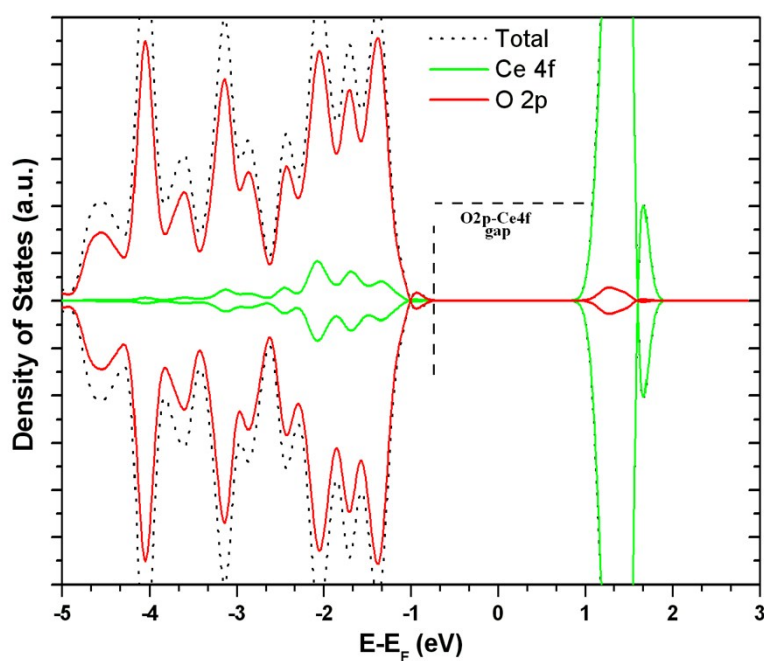


**Figure S4** - PDOS relative to the pure ceria ($CeO_2$) system calculated through DFT + U (U = 4.6 eV). The dotted lines correspond to the total DOS. The red lines represent the O2p states and green to Ce 4f states.
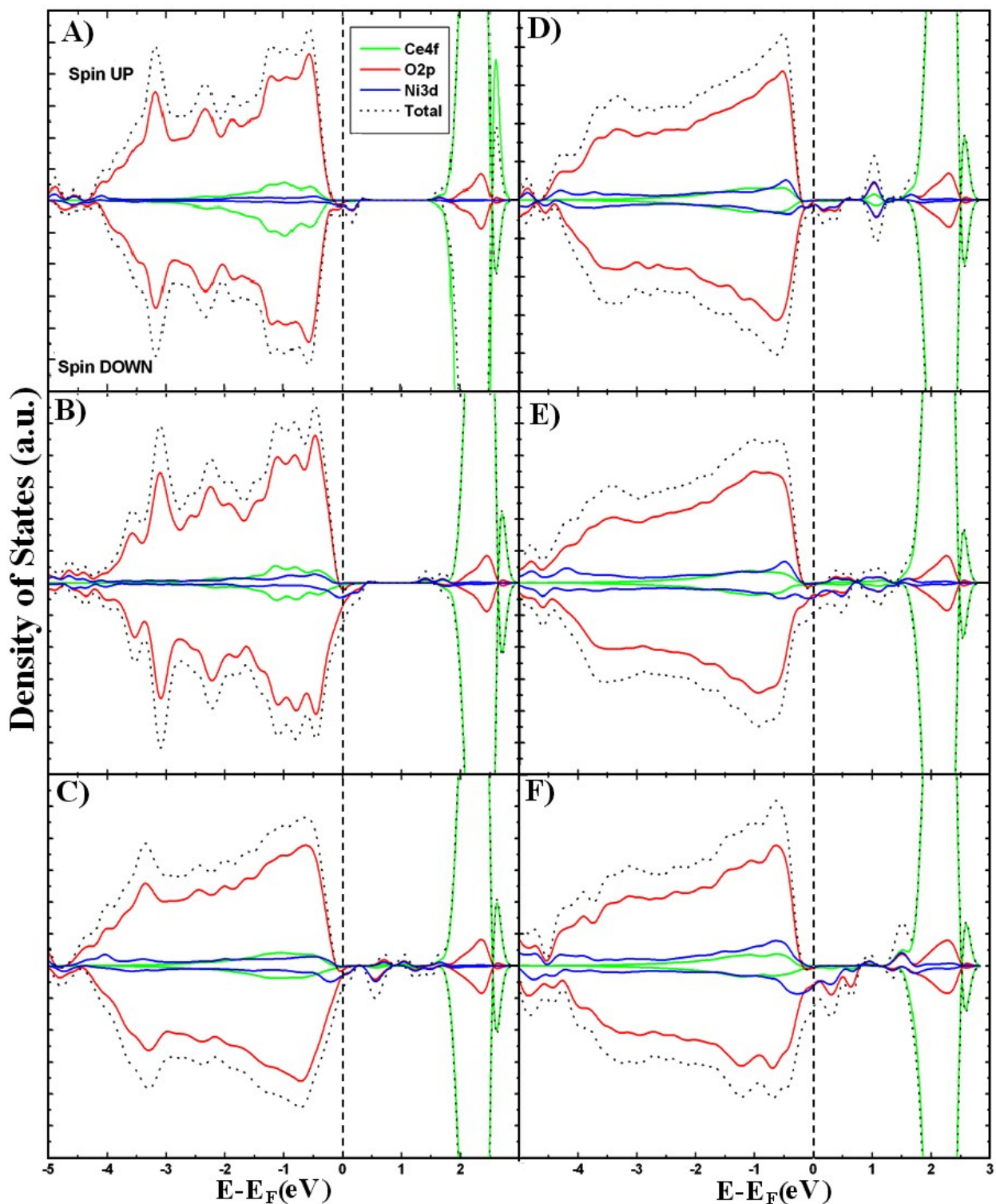
**Figure S5** - PDOS relative to the $NiCeO_\delta$ systems calculated through DFT + U (U = 4.6 eV). The dotted lines correspond to the total DOS. The red lines represent the O2p states, blue to Ni3d and green to Ce 4f states. For each system, spin-down and up states are shown below and above the abscissa. The systems corresponding to 3.12, 6.25, 9.37, 12.50, 15.62 and 18.75% of Ni doping are represented by the letters A, B, C, D, E and F, respectively.

Fig. S4 depicts the PDOS associated with the Ce 4f and O 2p states for the stoichiometric (pure) ceria. It is clear that the valence band is composed mostly by O 2p states and small contribution of Ce 4f states. On the other hand, the band located above the Fermi level is predominantly formed by the Ce 4f states and the calculated O2p-Ce4f band gap was found to be 2.201 eV. An analysis for the PDOS corresponding to the constituents of the Ni-doped ceria ($NiCeO_\delta$) solid solutions is shown in Fig. S5 (A-F). Similarly to the case of pure ceria, the valence band is also characterized by the presence of O 2p states with a lesser contribution of Ce 4f states. However, as expected, the presence of transition metal dopants induces the appearance of unoccupied electronic states known as gap states, localized between the empty Ce 4f levels and the top of the valence band (O 2p). Accordingly, a detailed analysis of the electronic structure of all solid solutions has identified as a general feature (unlike the case of the pure ceria) the presence of gap states in between the conduction and the valence bands. For example, an analysis for the PDOS of the system containing the least amount of Ni (3.12%) indicates a metal induced gap state slightly above the valence band characterized by the presence of localized Ni 3d and O2p (down) states. For higher amounts of dopant the gap states formed mainly by Ni 3d and O 2p states were found to be more delocalized.
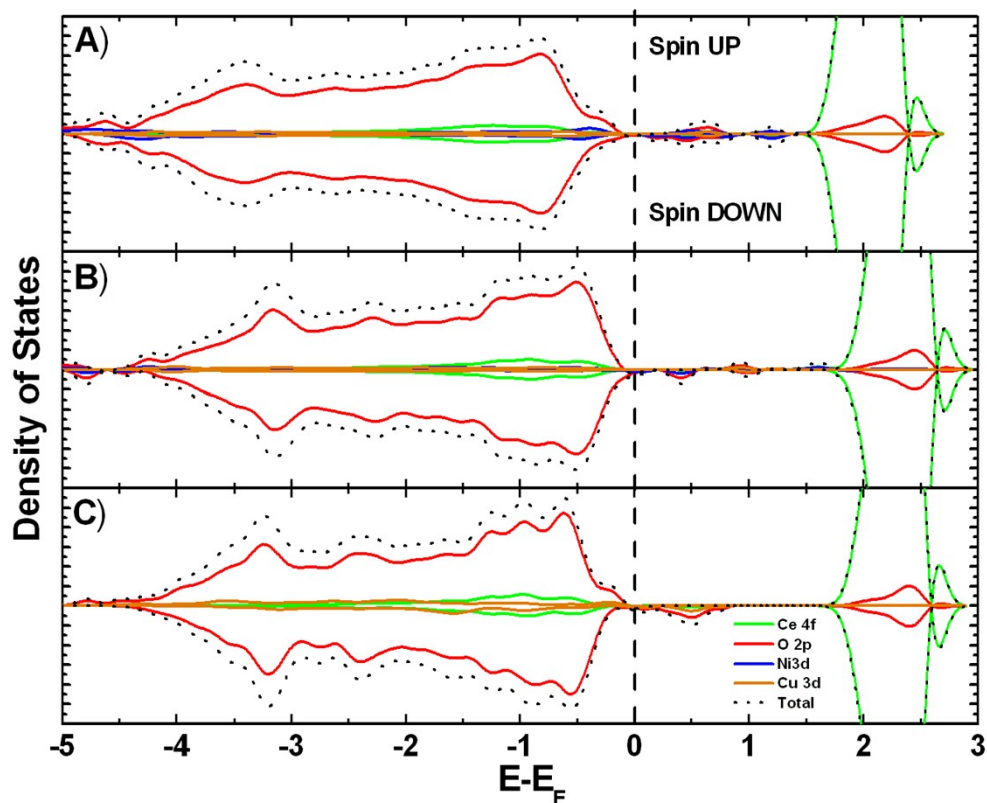
**Figure S6** - PDOS relative to the Cu-NiCeO$_\delta$ systems calculated through DFT + U (U = 4.6 eV). The dotted lines correspond to the total DOS. The red lines represent the O2p states, blue to Ni3d, orange Cu 3d and green to Ce 4f states. For each system, spin-down and up states are shown below and above the abscissa. The systems corresponding to "Ni (6.25%) + Cu (3.12%)", "Ni (3.12%) + (Cu 3.12%)" and " Cu(6.25%)" are represented by the letters A, B, C, respectively.

These tendencies are also present in the solid solutions containing Cu dopants, as seen in Fig. S6. Such a feature can be well understood if one considers that is impossible, in terms of comparison with a pure (ideal) ionic system with the CeO$_2$ crystal structure, for the O atoms of the doped structure to assume a (closed shell) O$^{2-}$ configuration since the total oxidation of Ni (Cu) produces only +2 (Ni$^{2+}$ and Cu$^{2+}$) instead of +4 configurations (Ce$^{4+}$) [SR 1]. A consequence of the substitution of Ce by Ni (Cu) in ceria is that the number of electrons (valence) available does not satisfy the amount electrons necessary to fill the O 2p states, which in turn might explain the presence of the unoccupied gap states. Furthermore, our DFT+U calculations indicate a solution with charge excess delocalized spatially on Ni

(Cu) atoms and (specially) nearest O neighbors, which in principle corroborate our assumptions. As can be observed in Figs. S7-S15, the net spin charge density is distributed mainly on the dopant centers as well as on their nearest neighbor O atoms.
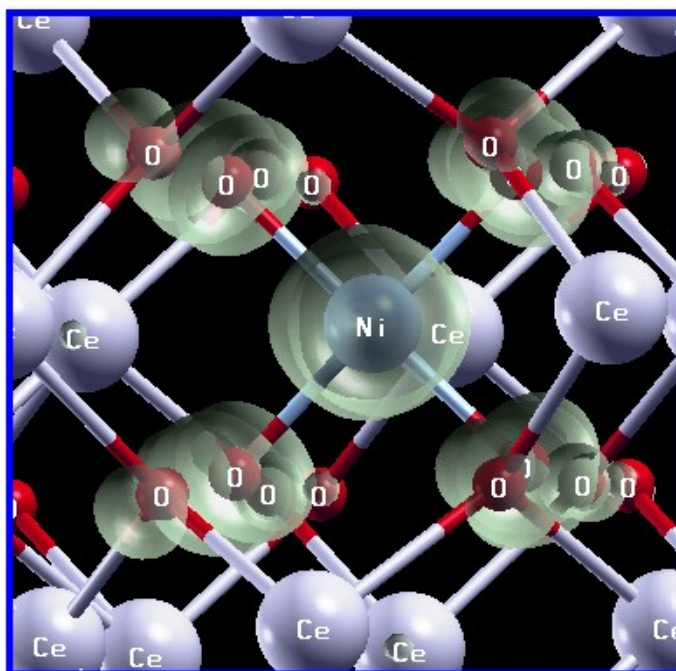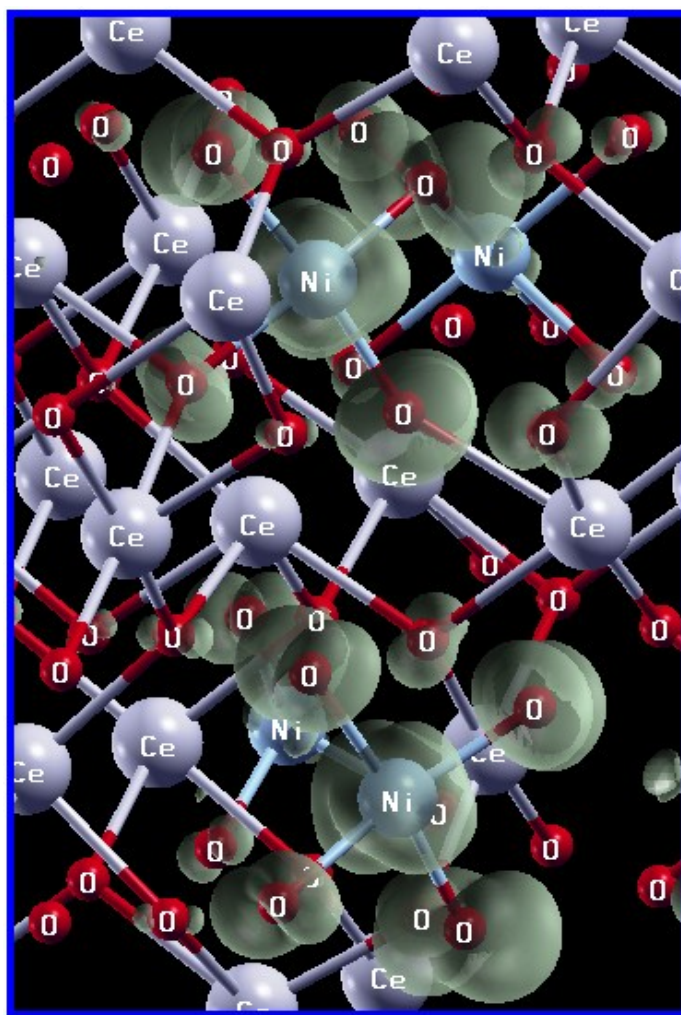


**Fig. S7 -** Spin density isocontours (0.003 electrons/$\text{Å}^3$) for the **Ni (3.12%)** doped ceria system (generated with XCrySDen [SR 12]).
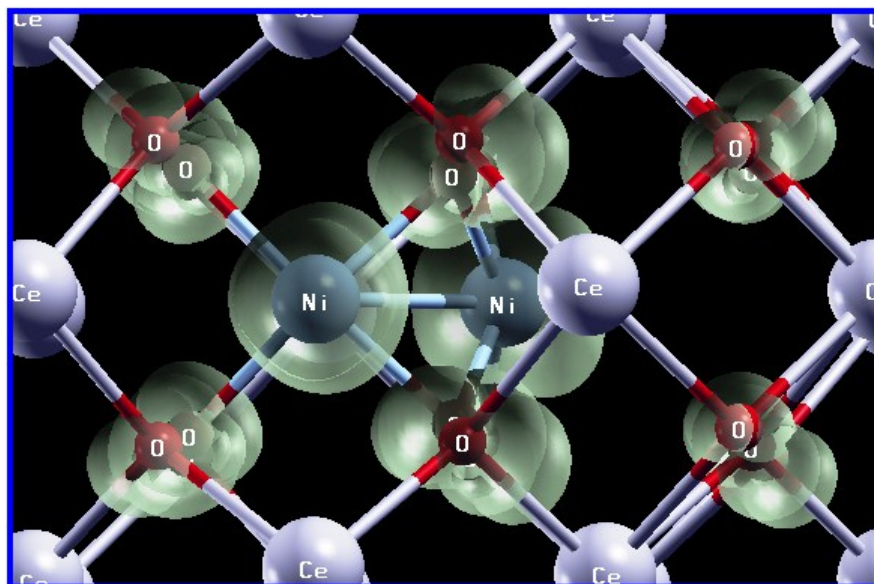
**Fig. S8 -** Spin density isocontours (0.003 electrons/Å$^3$) for the **Ni (6.25%)** doped ceria system.
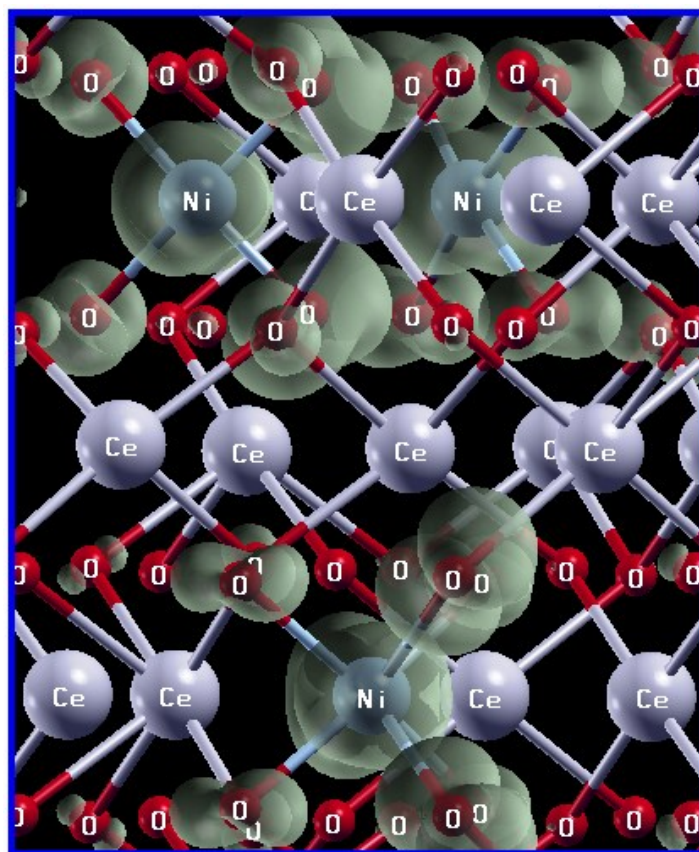


**Fig. S9 -** Spin density isocontours (0.003 electrons/Å$^3$) for the **Ni (9.37%)** doped ceria system.

**Fig. S10 -** Spin density isocontours (0.003 electrons/Å$^3$) for the **Ni (12.5%)** doped ceria system.
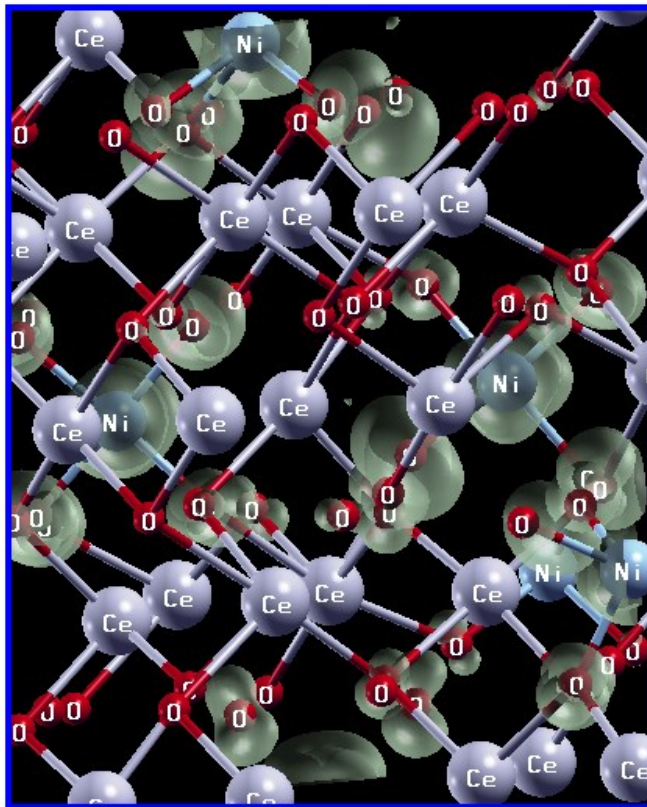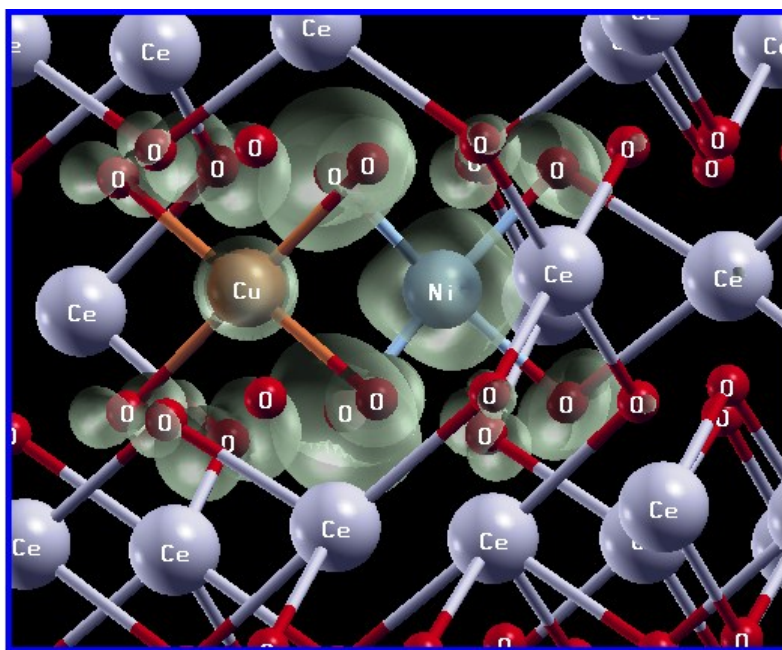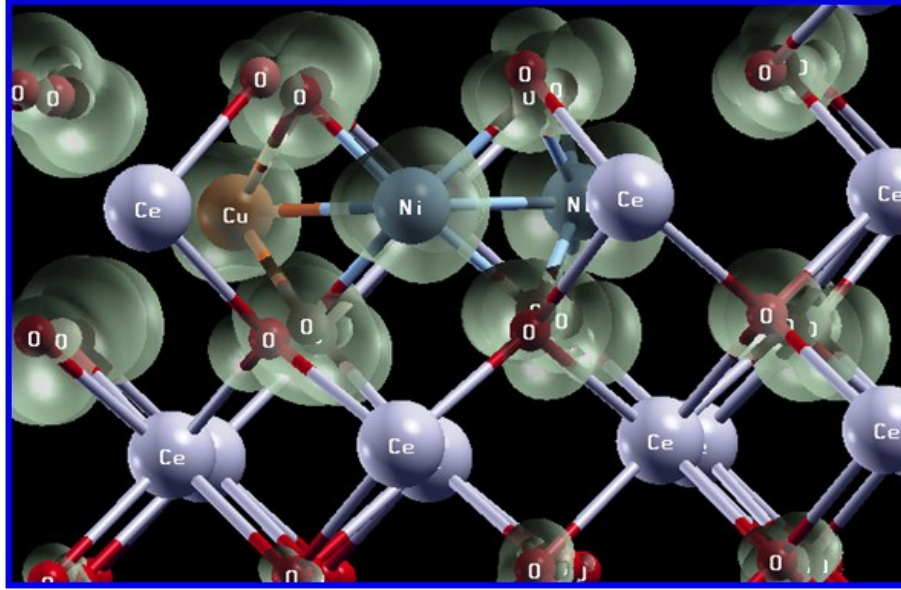
**Fig. S11 -** Spin density isocontours (0.003 electrons/Å$^3$) for the **Ni (15.62%)** doped ceria system.
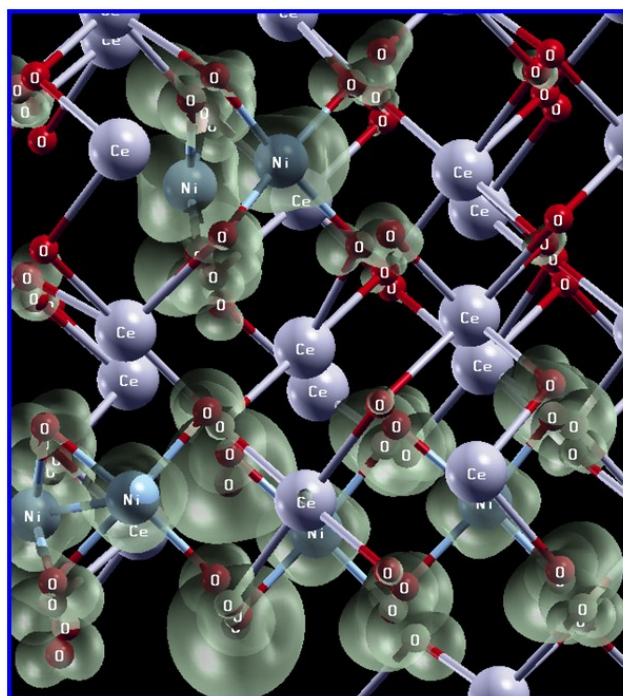


**Fig. S12 -** Spin density isocontours (0.003 electrons/Å$^3$) for the **Ni (18.75%)** doped ceria system.
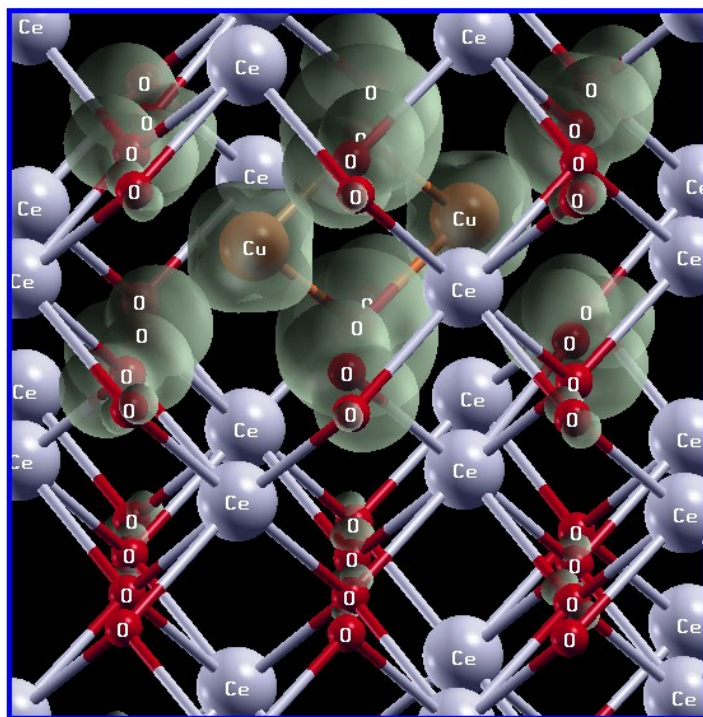
**Fig. S13 -** Spin density isocontours (0.003 electrons/Å³) for the **Cu (6.25%)** doped ceria system.



**Fig. S14 -** Spin density isocontours (0.003 electrons/Å³) for the **Ni(3.12%) + Cu(3.12%)** doped ceria system.

**Fig. S15 -** Spin density isocontours (0.003 electrons/Å$^3$) for the **Ni(6.25%) + Cu(3.12%)** doped ceria system.


## 3 – Löwdin Population Analysis

Additionally, the values of the partial charge population (Tables S3 and S4) calculated through the Löwdin population analysis for the solid solutions were explored in a range of +U terms. The analysis for the charges revealed that, contrarily to the formation energies, the charge distribution depend in some extent of the choice of the +U parameter for Ce. It can be observed a non-negligible variation of the Ce 4f Löwdin charges for values of +U from 0 up to 3.6 eV, and then a less intense variation until 5.0 eV. As a matter of fact, the choice of the +U parameter can influence on the correct representation of electronic states and electron localization effects in doped ceria [SR 11]. Overall, our results suggest that values equivalent or larger than 2.6 eV should be able to describe appropriately the electron localization in these systems, in good agreement with the literature [SR 1]. Furthermore, our the results also revealed that the oxidation state of the Ce atoms remains as +4 in all cases, while their substituting Ni species are in general slightly more ionic than the calculated reference state

(8.28 e⁻ for Ni in bulk NiO), since charge has to be transferred to O atoms in order to compensate in some extent the lack of formal charge left behind by $Ce^{4+}$ species.

**Table S3 - Löwdin Charges for the Ni-CeO$_2$ Solid Solutions as a Function of +U Terms**

| Ni (%) | U = 0 | | U = 0.6 | | U = 1.6 | | U = 2.6 | | U = 3.6 | | U = 4.6 | | U = 5.0 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ce(4f) | Ni(3d) | Ce(4f) | Ni(3d) | Ce(4f) | Ni(3d) | Ce(4f) | Ni(3d) | Ce(4f) | Ni(3d) | Ce(4f) | Ni(3d) | Ce(4f) | Ni(3d) |
| **Reference (pure ceria)** | 0.93 | 8.28 | 0.90 | 8.28 | 0.85 | 8.28 | 0.80 | 8.28 | 0.74 | 8.28 | 0.69 | 8.28 | 0.69 | 8.28 |
| **3.12** | 0.93 | 8.08 | 0.90 | 8.08 | 0.85 | 8.08 | 0.79 | 8.09 | 0.74 | 8.09 | 0.69 | 8.09 | 0.68 | 8.09 |
| **6.25** | 0.93 | 8.09 | 0.90 | 8.10 | 0.85 | 8.11 | 0.80 | 8.10 | 0.75 | 8.11 | 0.69 | 8.11 | 0.68 | 8.11 |
| **9.37** | 0.93 | 8.14 | 0.90 | 8.14 | 0.85 | 8.14 | 0.80 | 8.14 | 0.75 | 8.14 | 0.69 | 8.14 | 0.68 | 8.12 |
| **12.50** | 0.93 | 8.16 | 0.90 | 8.15 | 0.85 | 8.16 | 0.80 | 8.15 | 0.75 | 8.15 | 0.69 | 8.15 | 0.68 | 8.15 |
| **15.62** | 0.93 | 8.15 | 0.90 | 8.15 | 0.85 | 8.15 | 0.80 | 8.15 | 0.75 | 8.15 | 0.69 | 8.15 | 0.68 | 8.16 |
| **18.75** | 0.94 | 8.21 | 0.90 | 8.21 | 0.85 | 8.22 | 0.80 | 8.21 | 0.75 | 8.22 | 0.69 | 8.22 | 0.68 | 8.22 |

**Table S4 - Löwdin Charges for the Cu modified NiCeO$_\delta$ Solid Solutions as a Function of +U Parameters**

| | | U = 0.0 | U = 0.6 | U = 1.6 | U = 2.6 | U = 3.6 | U = 4.6 | U = 5.0 |
|---|---|---|---|---|---|---|---|---|
| **Ni(3.12%)** | Ce(4f) | 0.93 | 0.90 | 0.85 | 0.80 | 0.75 | 0.70 | 0.69 |
| **+** | Ni(3d) | 7.98 | 7.97 | 7.97 | 7.97 | 7.98 | 7.98 | 7.98 |
| **Cu(3.12%)** | Cu(3d) | 9.25 | 9.25 | 9.25 | 9.24 | 9.24 | 9.24 | 9.24 |
| **Ni(6.25%)** | Ce(4f) | 0.93 | 0.90 | 0.85 | 0.80 | 0.75 | 0.70 | 0.69 |
| **+** | Ni(3d) | 8.15 | 8.15 | 8.15 | 8.15 | 8.15 | 8.15 | 8.15 |
| **Cu(3.12%)** | Cu(3d) | 9.25 | 9.26 | 9.26 | 9.26 | 9.25 | 9.25 | 9.25 |
| | Ce(4f) | 0.93 | 0.90 | 0.85 | 0.80 | 0.79 | 0.69 | 0.68 |
| **Cu(6.25%)** | Ni(3d) | - | - | - | - | - | - | - |
| | Cu(3d) | 9.24 | 9.24 | 9.24 | 9.24 | 9.23 | 9.21 | 9.23 |

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TABLE with XPS data:

| Element | Orbital | Energy (eV) | Area (CPS. eV) | Atotal (CPS . eV) | Sens. Factor | % |
|---|---|---|---|---|---|---|
| | | | **Sample NiCeO** | | | |
| Ni | 2p 3/2 | 853,9 | 28770 | 43697,2 | 14,8 | 18,0 |
| | | 860,16 | 14927,2 | | | |
| Ce | 3d | 881,96 | 23918,6 | 92435 | 51,6 | 10,9 |
| | | 887,57 | 10516,4 | | | |
| | | 897,82 | 24944 | | | |
| | | 900,9 | 9322,6 | | | |
| | | 906,63 | 8879,5 | | | |
| | | 915,78 | 14853,9 | | | |
| O | 1s | 526,87 | 8086,4 | 25306,7 | 2,93 | 52,6 |
| | | 528,76 | 13885,8 | | | |
| | | 531 | 3334,5 | | | |
| C | 1s | 282,2 | 544,6 | 3033,3 | 1 | 18,5 |
| | | 284,6 | 1900 | | | |
| | | 288,5 | 588,7 | | | |
| | | | **Sample CuNiCeO** | | | |
| Cu | 2p 3/2 | 934 | 13490,4 | 16759,6 | 16,9 | 5,5 |
| | | 942,8 | 3269,2 | | | |
| Ni | 2p 3/2 | 855,9 | 19506,2 | 30307,2 | 14,8 | 11,4 |
| | | 862,2 | 10801 | | | |
| Ce | 3d | 883,73 | 31896,3 | 124246,7 | 51,6 | 13,5 |
| | | 889,58 | 17108,2 | | | |
| | | 899,77 | 31436,7 | | | |
| | | 902,7 | 12278,2 | | | |
| | | 908,73 | 11881,3 | | | |
| | | 917,78 | 19646 | | | |