Electronic Supplementary Information (ESI) for DFT+U and Quantum Monte Carlo study of electronic and optical properties of $AgNiO_2$ and $AgNi_{1-x}Co_xO_2$ delafossite

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1 Geometry for $AgNi_{1-x}Co_xO_2$

Obtaining accurate geometry is important in order to accurately estimate the electronic properties of doped systems. Because detailed geometry information is not available for $AgNi_{1-x}Co_xO_2$, we compare two different geometries in order to select one to use. A first geometry was obtained from full relaxation using PBE+U with ultra-soft pseudopotentials, and a second one was pristine stoichiometric $AgNiO_2$ geometry with Ni1 atoms simply replaced with Co for $AgNi_{1-x}Co_xO_2$. We performed DMC total energy calculations on these two geometries in order to find the more stable structure with lower fixed-node DMC energy. DMC calculations were done with a 580 electrons supercell and the estimated DMC energy for the DFT-relaxed $AgNi_{1-x}Co_xO_2$ geometry and for the pure $AgNiO_2$ geometry are -9049.547(11) eV/f.u. and -9049.569(10) eV/f.u., respectively. It is interesting, and perhaps surprising, that the pure $AgNiO_2$ geometry has a lower fixed-node DMC energy, which implies that the $AgNiO_2$ structure is more stable than the PBE+U-relaxed $AgNi_{1-x}Co_xO_2$ structure. Therefore, it is necessary to develop and use other geometry optimization methods for the delafossites. That will be the subject of future work; for the present work, we decided to use the pure $AgNiO_2$ structure for $AgNi_{1-x}Co_xO_2$. does not produce a well-optimized geometry for $AgNi_{1-x}Co_xO_2$.

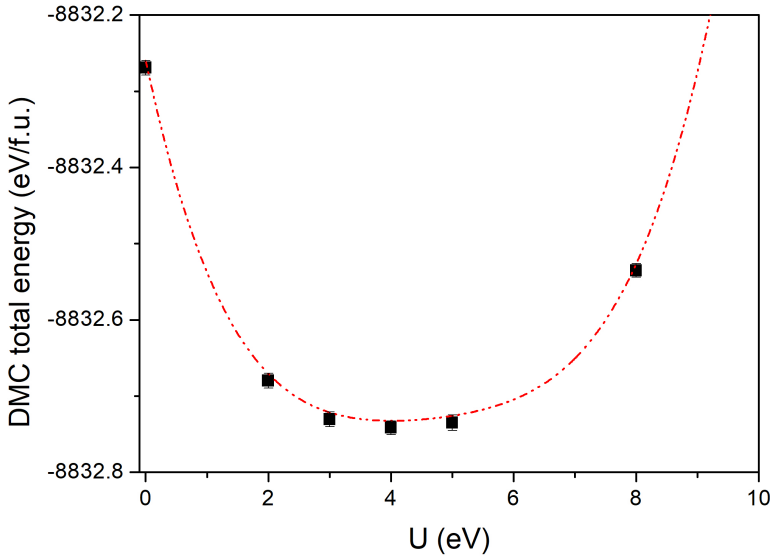

Fig. 1 DMC total energy of $AgCoO_2$ as function of Hubbard U in the PBE+U trial wavefunction..

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2 U scanning for $AgCoO_2$

The optimal value of U for a Co atom in $AgNi_{1-x}Co_xO_2$ was chosen by scanning value of U in 2H-$AgCoO_2$ structure. DMC calculation for scanning U was performed in 576 electrons cell within PBE+U trial wavefunction. As seen in Figure 1, the optimal value of U for a Co atom was obtain through a quartic fit to DMC total energies and were estimated to be 4.0(1) eV.

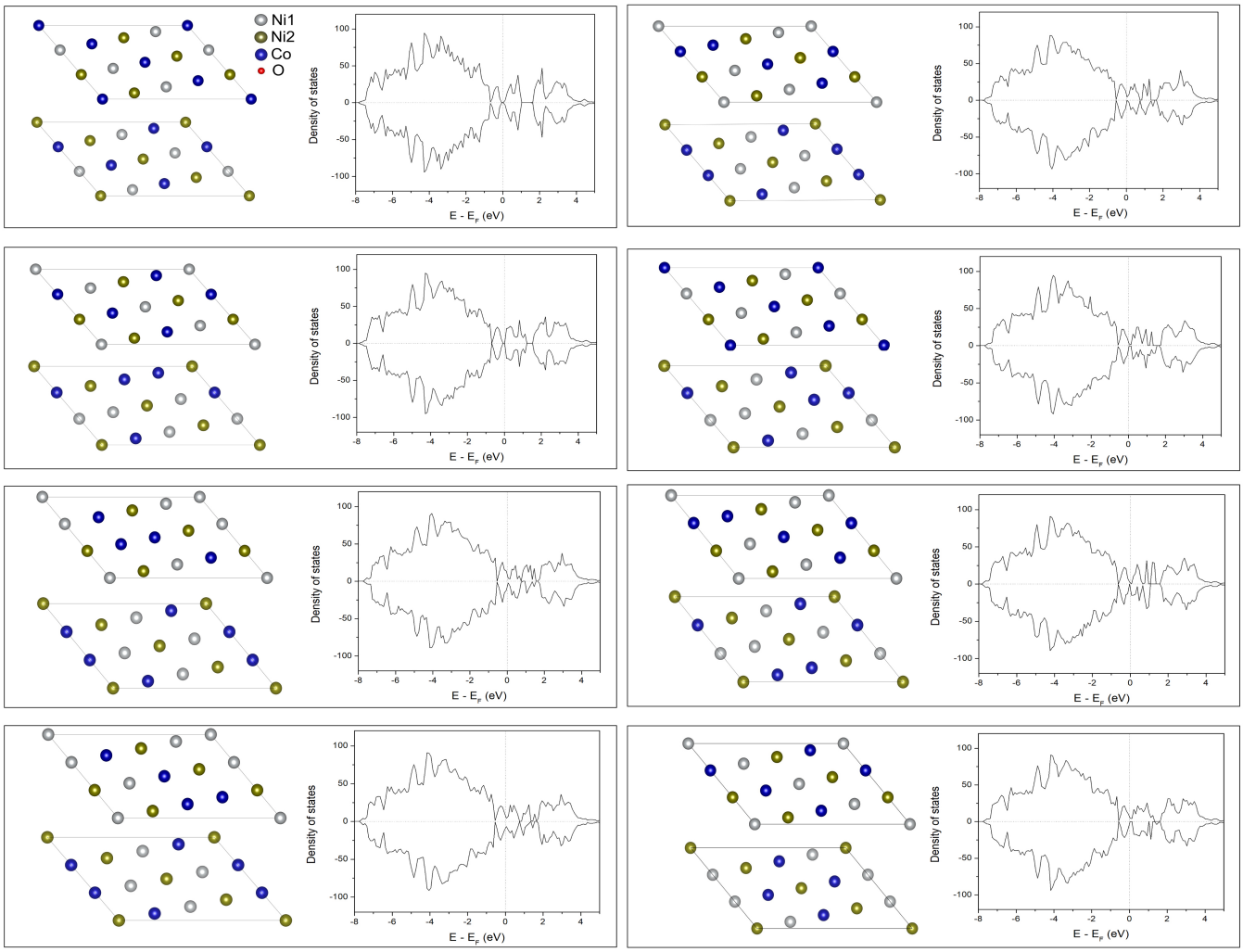

Fig. 2 Upper and lower Co-doped NiO_2 layers and total density of states for selected 8 phases of 96 atoms cell of $AgNi_{0.66}Co_{0.33}O_2$.

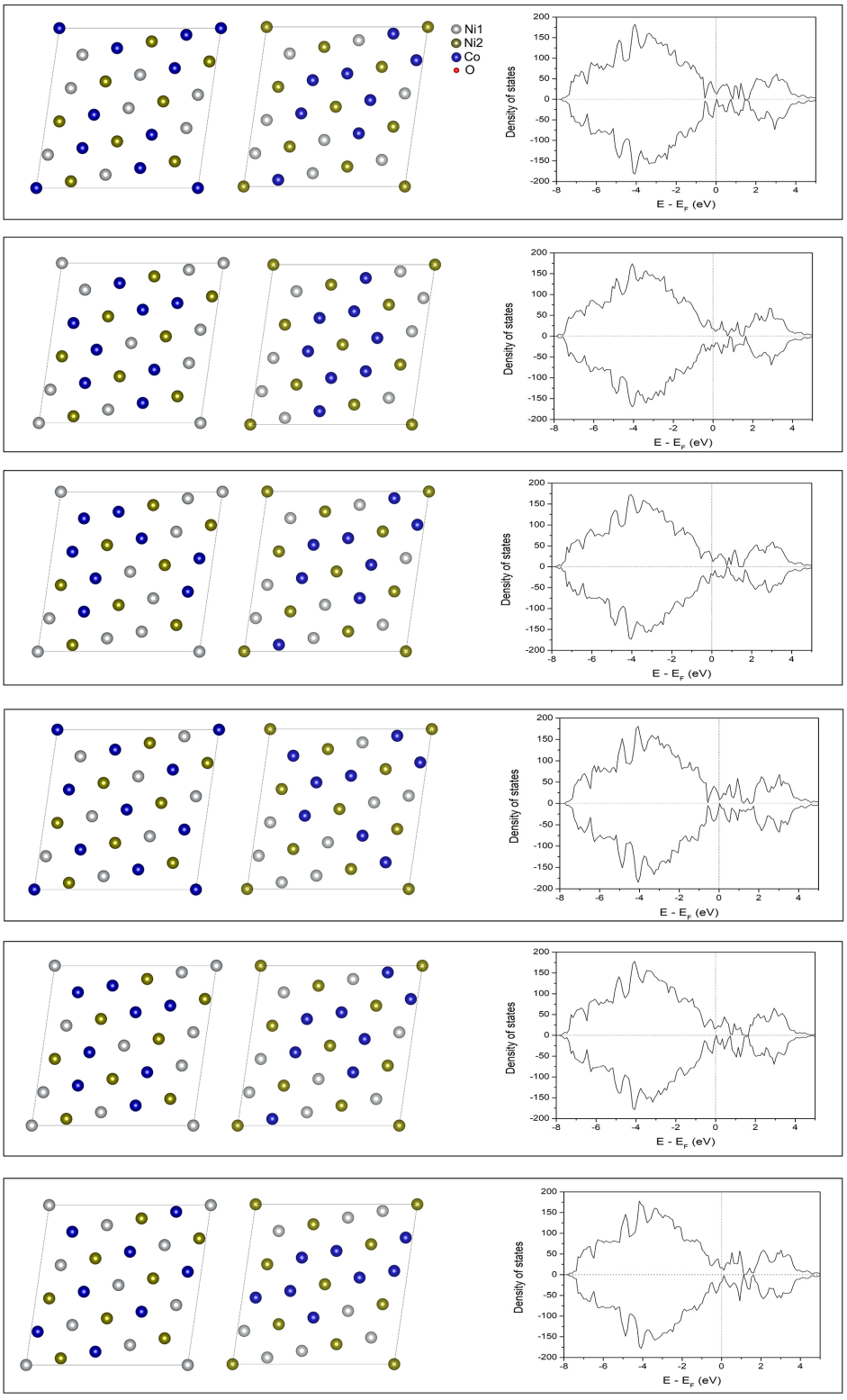

Fig. 3 Upper and lower Co-doped NiO_2 layers and total density of states for selected 6 phases of 192 atoms cell of $AgNi_{0.66}Co_{0.33}O_2$.