SUPPLEMENTARY INFORMATION

A first principles study of the effect of (111)-strain on octahedral rotations and structural phases of $LaAlO_3$

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ORBITAL SPLITTING

As stated in the main manuscript the bottom of the conduction band consists of e_g orbitals of the La $5d$ states. In FIG S1, we show that these orbitals are lower in energy as compared to the t_{2g} orbitals due to the dodecahedral coordination of the 5d states where the t_{2g} orbitals have their lobes pointing towards the oxygen anions, while the lobes of the e_g orbitals are in between the oxygen. For compressive (001)-strain we see that the e_g orbitals are split with the $d_{x^2-y^2}$ orbital reduced in energy as the top and bottom oxygens are pushed towards the nodes, while the d_{z^2-r} orbital is increased in energy as the oxygens are pushed towards the lobes of the d_{z^2-r} orbital. For tensile (001)-strain the situation is reversed and the $d_{x^2-y^2}$ state is increased in energy and the d_{z^2-r} is reduced in energy. However, for the trigonal distortion from (111)-strain none of the oxygens are being pushed explicitly towards the nodes or the lobes of the different e_g orbitals, thus the e_g states are degenerate under (111)-strain.[1] (111)-strain does however affect the crystal field splitting of the t_{2g} orbitals, as they can be decomposed into the trigonal a_{1g} and e_g' orbitals,[1] however these orbitals are not at the bottom of the conduction band for $LaAlO_3$, and thus does not affect the band gap.

DENSITY OF STATES FROM THE HYBRID FUNCTIONAL CALCULATIONS

Figure S2 shows the density of states for representative values of strain as calculated with the HSE-sol hybrid functional.[2] As shown, the band gap of the unstrained system increases from 3.4 eV calcultated with PBE-sol to 5.0 eV, significantly closer to the experimental bulk value of 5.6 eV.[3] Still, we observe here that the bottom of the conduction band consist of La $5d$ states, with the La $4f$ states is centered at the same energy window as the $5d$ t_{2g} orbitals, and thus do not affect the band gap. The Al s and p states are even higher in energy, which is not suprising given that the band gaps of the binary oxides La_2O_3 and Al_2O_3 (corundum) are in the order of 6 and 8.8 eV, respectively.[4] We further confirm the main findings from the PBE-sol calculations, the changes in band gap observed for (001)-strain is dominated by different splitting of the e_g states. While as the e_g states are degenerate for (111)-strain, the changes in the band gap here are dominated by the weaker effect of changes in the interatomic distances.

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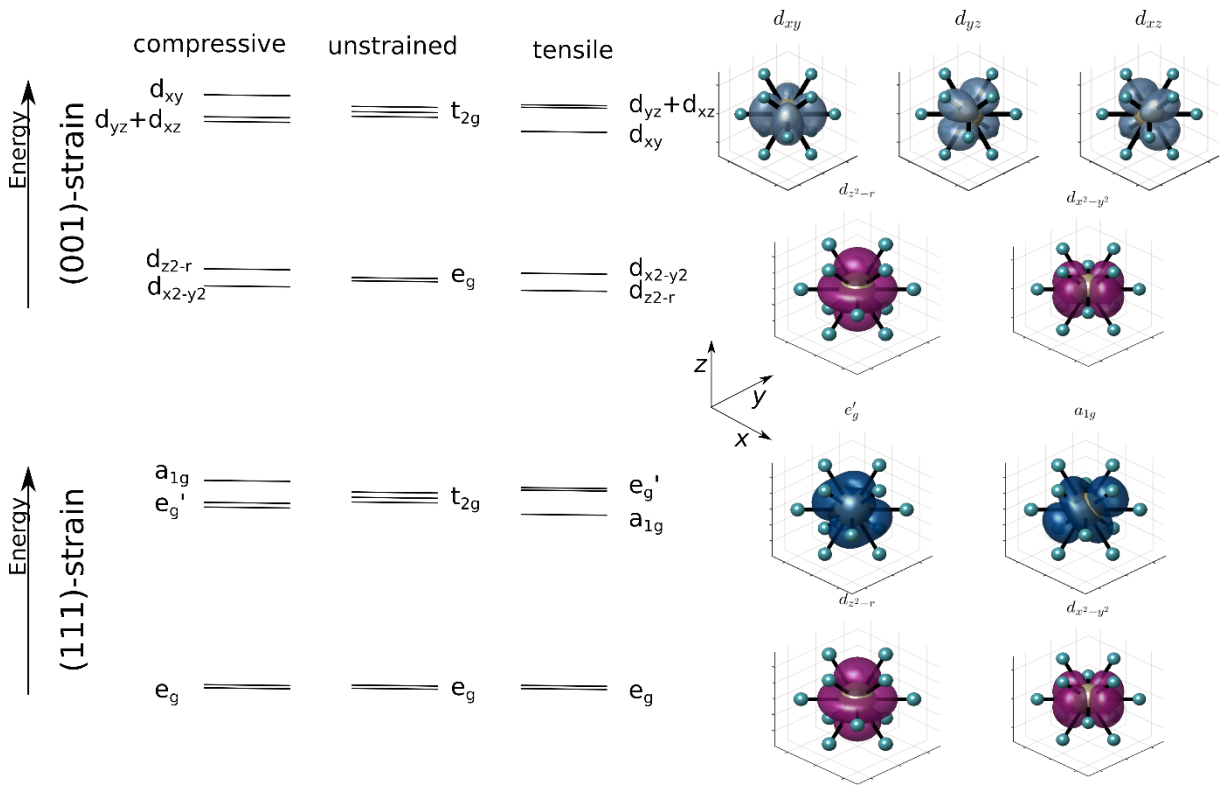

Figure S1, visualization of the different dodecahedrally coordinated La_{3d} orbitals and how they are affected by the crystal field splitting. The orbitals plotted is the $3d$ orbitals, while it is the 5d orbitals which are at the bottom of the conduction band, however going from $3d$ to $5d$ only adds additional radial nodes, and thus do not affect the character of the orbital splitting.

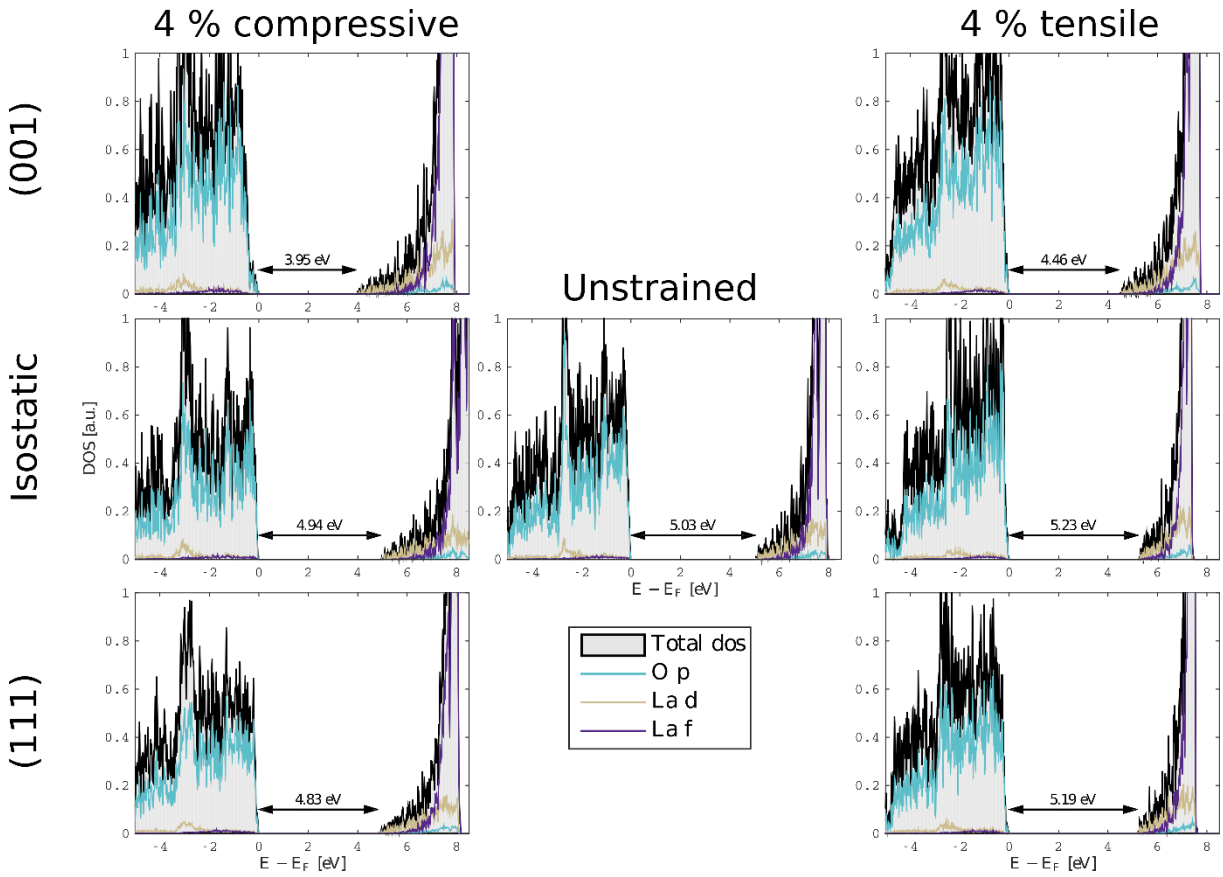

FIG S2, the density of states (DOS) calculated with the HSE-sol hybrid functional for different strain cases. For 4 % compressive (111)-strain the three degenerate phases have similar DOS and band gap, thus only the results for the $C2/c$ phase is shown.