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 5$d$ 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 5$d$ 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 $d_{z^2}$ orbital is increased in energy as the oxygens are pushed towards the lobes of the $d_{z^2}$ orbital. For tensile (001)-strain the situation is reversed and the $d_{x^2-y^2}$ state is increased in energy and the $d_{z^2}$ 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. However, (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, 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. As shown, the band gap of the unstrained system increases from 3.4 eV calculated with PBE-sol to 5.0 eV, significantly closer to the experimental bulk value of 5.6 eV. Still, we observe here that the bottom of the conduction band consist of La 5$d$ states, with the La 4$f$ states is centered at the same energy window as the 5$d$ $t_{2g}$ 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$_2$O$_3$ and Al$_2$O$_3$ (corundum) are in the order of 6 and 8.8 eV, respectively. 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.

REFERENCES

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 3$d$ orbitals, while it is the 5$d$ orbitals which are at the bottom of the conduction band, however going from 3$d$ to 5$d$ 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.