

Supporting Information

From borophene polymorphs towards a single honeycomb borophane phase: reduction of hexagonal boron layers on Al(111)

Pietro Biasin,^a Mandana Safari,^b Elena Ghidorsi,^a Stefania Baronio,^a Mattia Scardamaglia,^c Alexei Preobrajenski,^c Stefano de Gironcoli,^{b,d} Stefano Baroni,^{b,d} Erik Vesselli^{a,e,f,*}

^aDepartment of Physics, University of Trieste, Trieste 34127, Italy.

^bScuola Internazionale Superiore di Studi Avanzati, Trieste 34136, Italy.

^cMAX IV Laboratory, Lund University, 22100 Lund, Sweden.

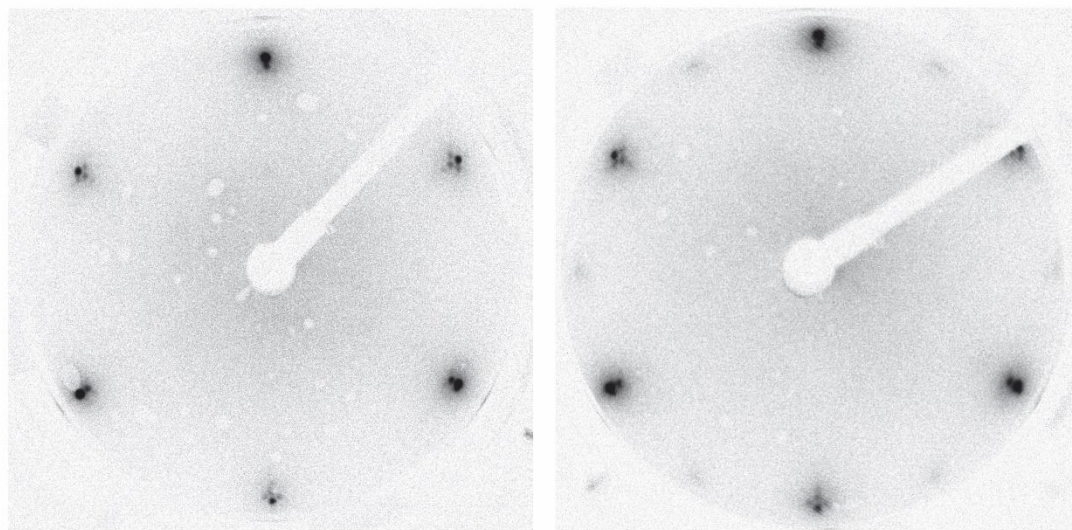
^dIstituto Officina dei Materiali, SISSA Unit, CNR, Trieste 34136, Italy.

^eTASC Laboratory, Istituto Officina dei Materiali, CNR, Trieste 34149, Italy.

^fCenter for Energy, Environment and Transport Giacomo Ciamician, University of Trieste, Trieste 34127, Italy.

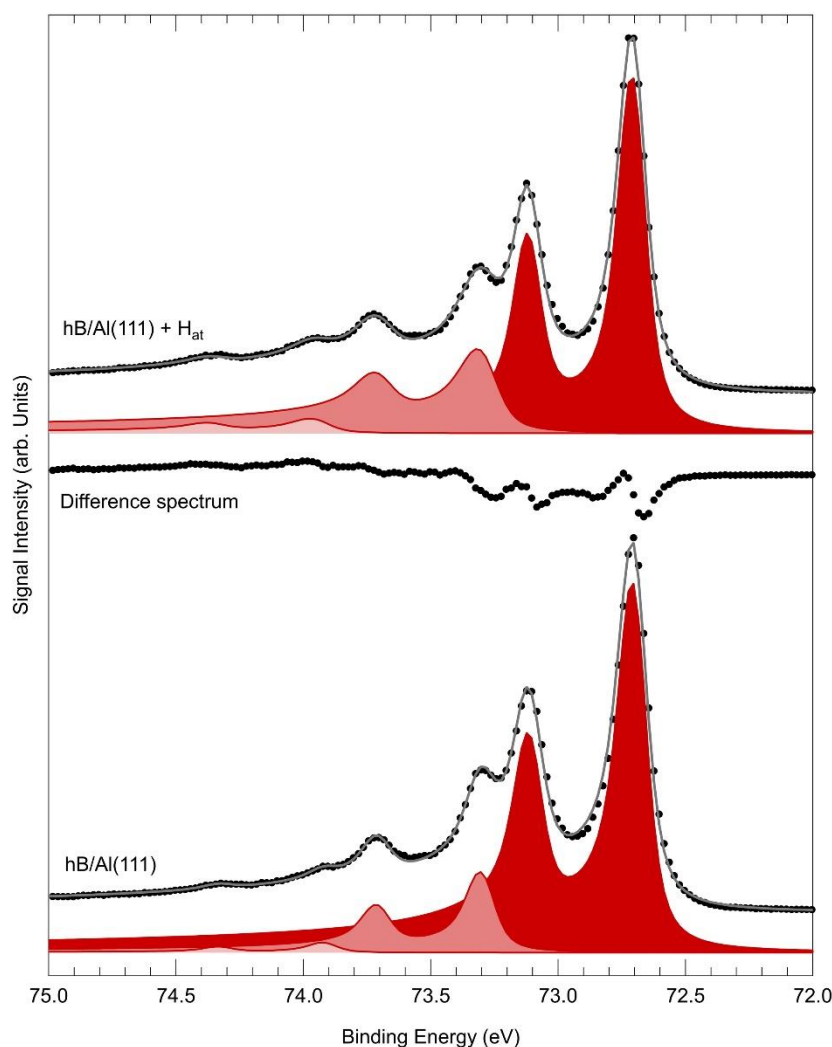
*e-mail: evesselli@units.it

Figure S1.



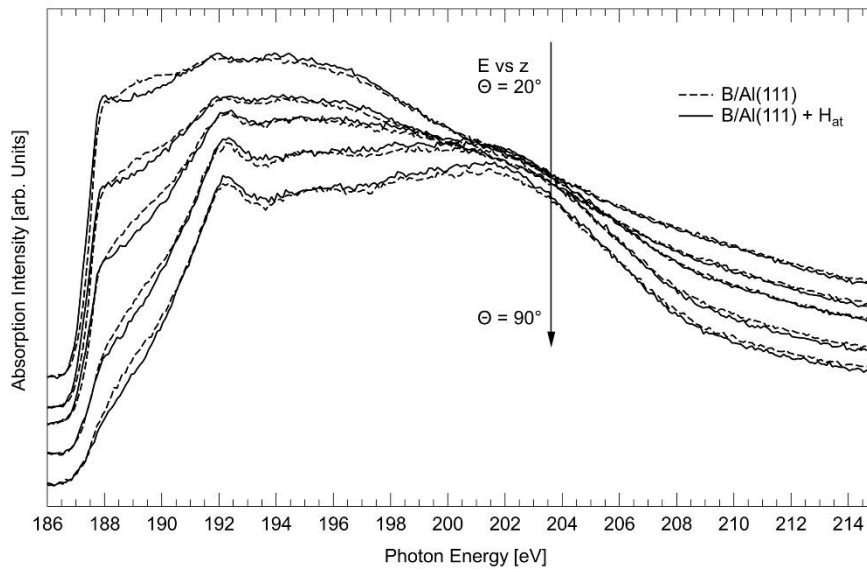
Raw LEED patterns (48 eV) of the bare hB/Al(111) phase with deficient (< 2.0 ML, left) and close to stoichiometric (2.0 ML, right) B coverage, so that in the latter case the presence of a second phase (rotated by 30°) can be observed prior to completion of the first layer. The B coverage expressed in ML (monolayers) is referred to the terminal Al(111) surface, where 1 ML corresponds to one B ad-atom for each surface Al atom.

Figure S2.



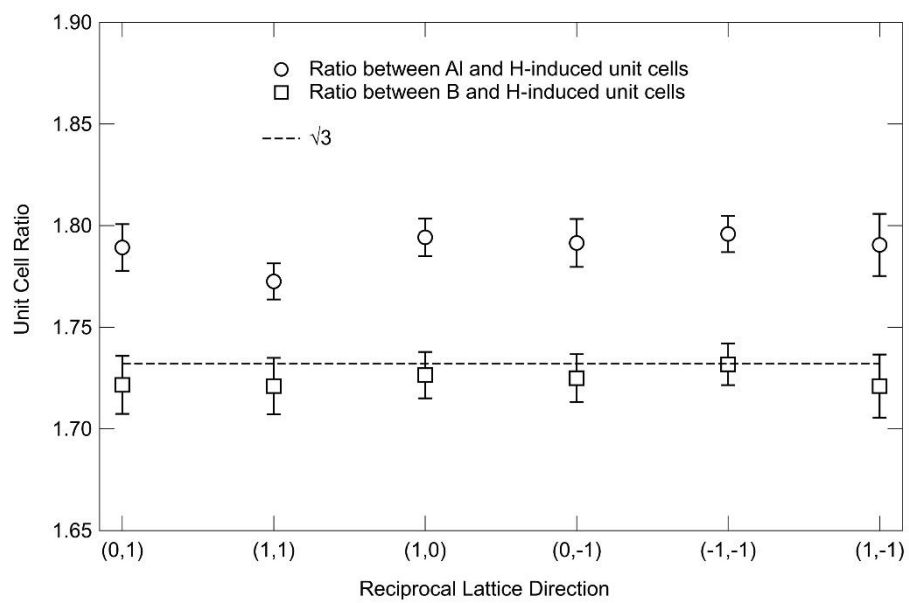
Al 2*p* XPS spectra ($h\nu = 155$ eV) of the hB/Al(111) layer prior (bottom) and after (top) hydrogenation. Data points (black dots) are plotted together with the best fit (grey lines), the deconvolution profiles (colored profiles), and the raw difference spectrum (middle). The best fit was obtained globally on an extended data set that included spectra collected with photon energies ranging from 145 to 155 eV. In order to reduce the number of degrees of freedom, important constraints were imposed on the fitting parameters, so to yield solid results even in the framework of a model. In particular, the spin orbit split energy was globally optimized (0.41 eV) and the $2p_{1/2}$ to $2p_{3/2}$ intensity ratios were fixed to 1:2. Also the lineshape was globally optimized (Lorentzian width, asymmetry parameter) while the gaussian width was optimized separately for the main (bulk) and B-related components. The best fit gaussian and asymmetry parameters are different for the pristine and hydrogenated AlB₂ components. Finally, it was not possible to resolve with statistical significance any clean Al surface and B-Al interface component close to the main feature at 72.70 eV. The fit of the bare hB/Al(111) spectra is in full agreement with previous literature [ACS Nano 15 (2021) 15153].

Figure S3.



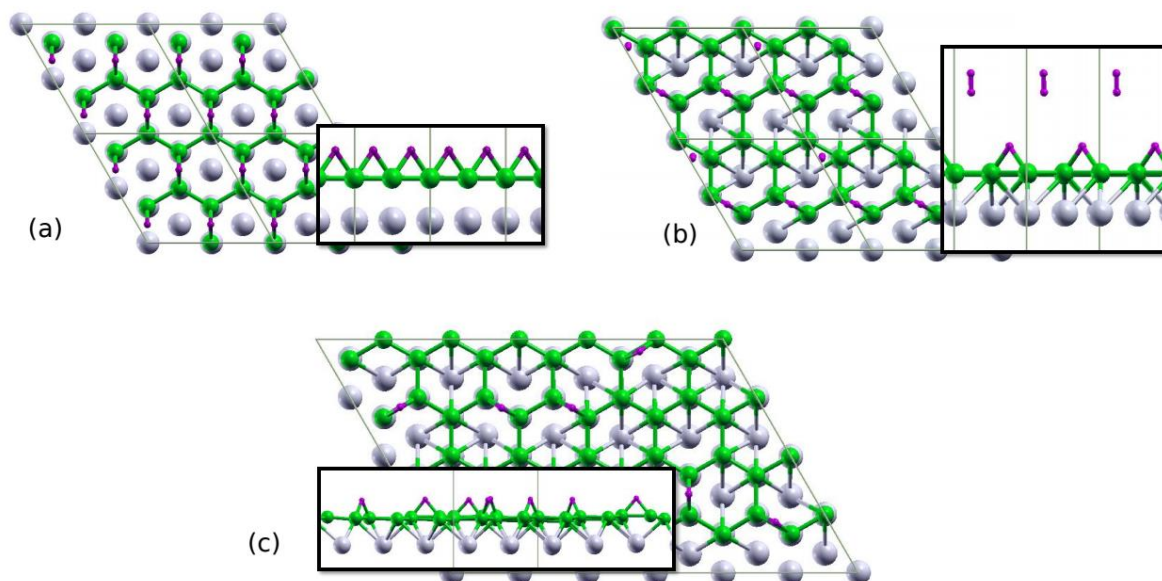
B edge NEXAFS spectra before (dashed lines) and after (solid lines) exposure of the B/Al(111) layer to atomic hydrogen at room temperature. A dichroic behavior is observed as a function of Θ , defined as the angle between the electric field of the impinging, linearly polarized radiation and the normal direction with respect to the sample surface.

Figure S4.



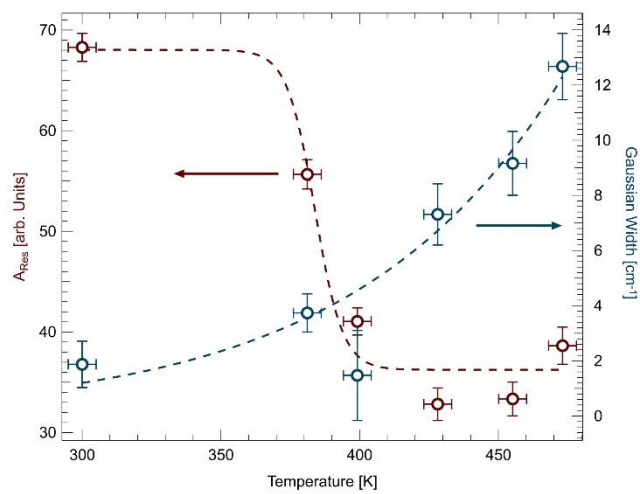
Compatibility of the H-induced unit cell size with the proposed $(\sqrt{3} \times \sqrt{3})$ -R30° superstructure referred to the hB phase obtained from LEED.

Figure S5.



We report here the most significant H-hB/Al structures that we obtained by genetic algorithm methods. The saturated (1 ML) structure in (a) is energetically slightly less stable than the layer in (b), where part of the H atoms was desorbed into the gas phase as H₂ molecules, leaving an average surface coverage of the order of 1/6 ML. The direct lateral interactions, however, are not sufficient to drive the ordering of the H network, neither if we enlarge the calculation cell (c), meaning that a substrate-drive mechanism is expected.

Figure S6.



Temperature-dependent IR-Vis SFG amplitude (red, left) and gaussian width (blue, right) of the vibronic resonance observed at 1934 cm^{-1} upon exposure of the hB/Al(111) layer to atomic hydrogen.