Supplementary Information for: On the Exfoliation and Anisotropic Thermal Expansion of Black Phosphorus.

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I. FURTHER COMPUTATIONAL DETAILS

All quantum chemical calculations were performed within the framework of Density Functional Theory (DFT), using the the CRYSTAL17 code[1] and the VASP5.4 software suite.[2, 3]

CRYSTAL17 calculations were carried out using Γ-centered k-meshes according to the Monkhorst-Pack method to sample of the first Brillouin zone (FBZ).[9] The applied TZVPP level basis set is reported in Ref. [10]. A larger basis set, named TZVPP2 as reported in Ref. [4] has been also used for evaluating any basis set deficiency. From the results in Table S1, and from Figures S4, S6 and S1, it is clear that the use of a different basis set has a small effect on the absolute values, and almost negligible on general trends. Significant differences in the thermal expansion are observed only at temperatures higher than 400 K. The five thresholds T_i, which control the truncation criteria of the Coulomb and exchange infinite lattice series, have been set to 8 (T1-T4) and 16 (T5).[11]. In Figure S2 we show that the PBE0-D3(zd) yields almost identical results on the thermal expansions as the PBE0-D3(zd,atm) variant.

VASP calculation were carried out by using hard pseudopotentials (PAW_PBE P 06Sep2000), an energy cutoff of 1000 eV. 8x8x8 Gamma-centered k-points were used for the bulk, and 8x8x1 for the layer calculations. In the latter case, a c-axis of 25 Å was chosen, which was tested to be converged with respect to 40 Å. An 'accurate' FFT grid was adopted.

The choice of the supercell expansion matrix[13] and the electronic k-meshes are reported in Tab. S2.

II. ADDITIONAL RESULTS

As a complement to the results reported in the main text, in the following some additional results are reported in Figures S3, S5, S7, S8. These include the thermal expansion coefficients α_V and α_L, the temperature dependence of the bulk modulus, and the heat capacity C_p. These plots show also the dependence on the supercell size and shape and, as previously mentioned, the stability of the results with respect to a change in the basis set choice. All results, if not differently stated, have been obtained at the PBE0-D3(zd, atm) level.

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Table S1: Structural data and exfoliation energy of black-P for different first-principles methods. Some theoretical and experimental data available in literature are reported too.

basis set	method		a	b	c	V	E_{exf}^{rlx}
	functional	D3 version	(Å)			(Å^3/atom)	(meV/atom)
TZVPP2[4]	PBE0-D3	zd	3.29	10.57	4.41	19.2	-102.3
		zd+atm	3.29	10.62	4.44	19.4	-86.3
		bj	3.28	10.15	4.23	17.6	-145.1
		bj+atm	3.28	10.18	4.25	17.7	-125.8
TZVPP[4]		zd	3.30	10.61	4.42	19.4	-101.5
		zd+atm	3.32	10.66	4.44	19.5	-86.0
		bj	3.30	10.20	4.25	17.9	-144.4
		bj+atm	3.30	10.25	4.27	18.1	-125.1
	PBE	–				20.7	-12.9
MINIX	HF-3c	zd	3.36	11.07	4.63	21.5	-94.1
		zd+atm	3.36	11.11	4.64	21.7	-81.1
		bj	3.31	10.32	4.30	18.3	-143.3
		bj+atm	3.31	10.36	4.31	18.4	-124.8
def2-mSVP	PBEH-3c	zd+atm	3.32	10.21	4.37	18.5	-110.8
		bj+atm	3.32	10.16	4.33	18.2	-129.2
def2-mSVP	HSE-3c	zd+atm	3.32	10.18	4.34	18.4	-115.5
		bj+atm	3.32	10.08	4.27	17.9	-144.2
def2-mTZVP	B97-3c	zd+atm	3.33	10.70	4.62	20.5	-120.9
		bj+atm	3.31	9.93	4.12	16.9	-217.6
Plane Wave cutoff=1 KeV	PBE	–	3.31	11.33	4.57	21.37	-9.5
		D3 (zd+atm)	3.31	10.74	4.46	19.78	-73.8
		TS	3.31	10.90	4.43	19.99	-92.6
		MBD	3.31	10.52	4.36	19.00	-77.8
	SCAN	–	3.29	10.95	4.53	20.4	-36.2
		D3 (zd+atm)	3.29	10.82	4.50	20.0	-63.9
		D3 (bj+atm)	3.29	10.73	4.47	19.7	-72.8
Literature							
Exp.	powder diffr.	Ref. [5]	3.31	10.48	4.38	19.0	
	powder diffr.[c]		3.31	10.42	4.36	18.8	
	TOF neutron diffr.	Ref. [6]	3.31	10.47	4.37	19.0	
Theo.	QMC[a]	Ref. [7]					-80
	rCCD[b]	Ref. [8]					-92
	p-LMP2	Ref. [4]	3.27	10.42	4.36	18.6	

[a] Starting from the experimental structural data at room temperature.
[b] Starting from the p-LMP2 optimised data.
[c] values at 0 K temperature, estimated by correcting the results in the line above for temperature effects as estimated by the QHA method in this paper.

Table S2: The choices of the Super Cells (SCs) and **k** sampling for each calculation.

Parameters	Supercells		
	2x2x2	conv[a]	3x3x3
SC expansion matrix	$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	$\begin{pmatrix} 3 & -3 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	$\begin{pmatrix} 3 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 3 \end{pmatrix}$
k-mesh	4x4x4	3x3x3	2x2x2

[a] The SC expansion matrix of the black phosphorus has been set in order to perform the calculations on the crystallographic unit cell and not on the primitive unit cell.

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[13] A supercell is obtained by defining the new unit cell vectors as linear combinations of the primitive cell unit vectors.[11]

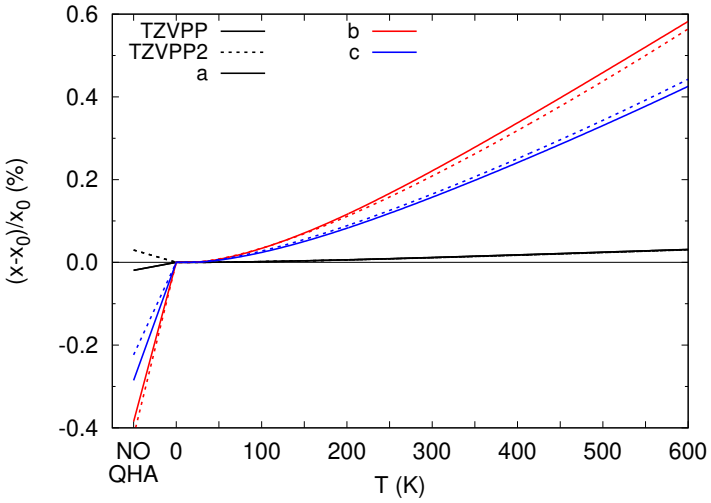

Figure S1: Relative lattice parameter thermal expansion as obtained for the 2x2x2 supercell with TZVPP and TZVPP2 basis sets, respectively.

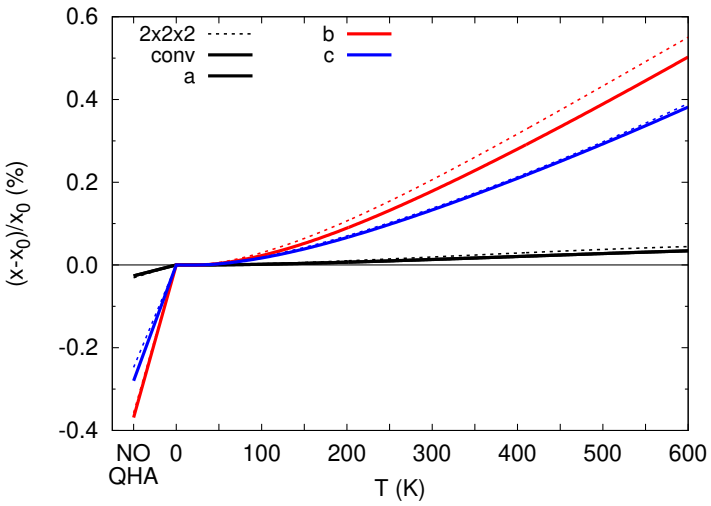

Figure S2: Relative lattice parameter thermal expansion as obtained for the 2x2x2 and conv supercell with PBE0-D3(zd) functional.

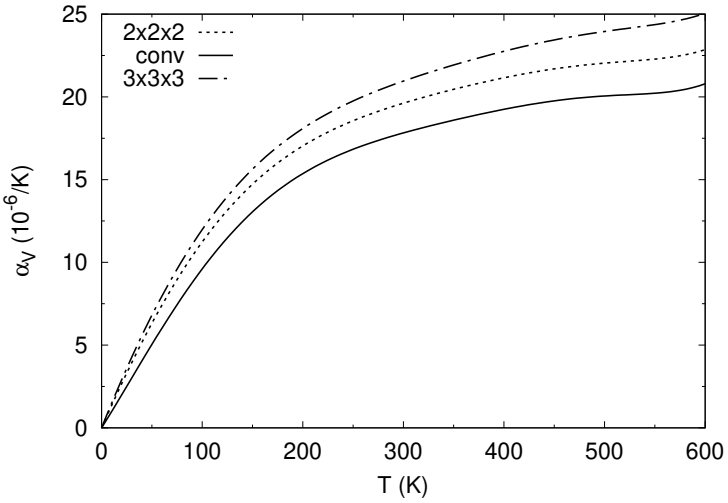

Figure S3: Volume thermal expansion coefficient as obtained with the TZVPP basis set for the 2x2x2, conv, and 3x3x3 supercells, respectively.

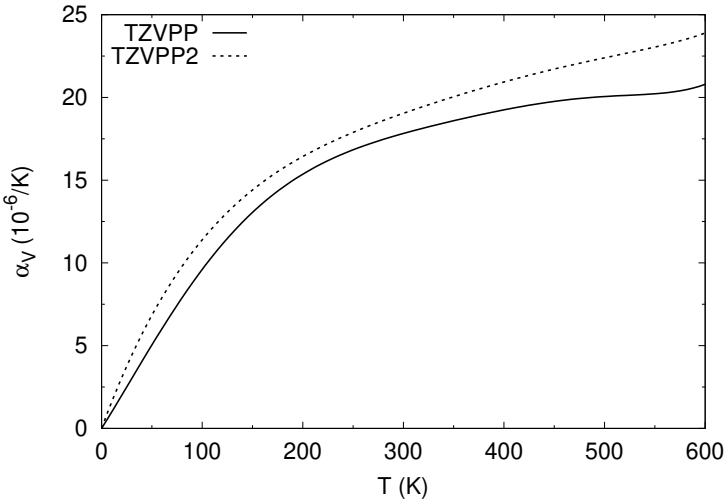

Figure S4: Volume thermal expansion coefficient as obtained for the 2x2x2 supercell with the TZVPP and TZVPP2 basis sets, respectively.

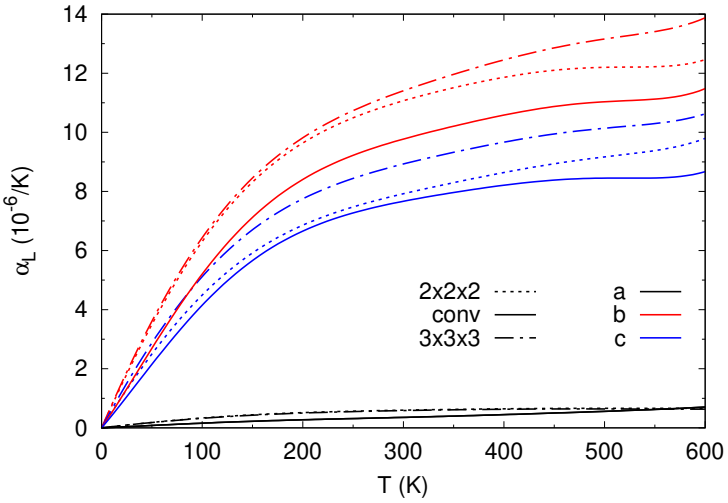

Figure S5: Linear thermal expansion coefficients of each lattice parameter as obtained with the TZVPP basis set for the 2x2x2, conv, and 3x3x3 supercells, respectively.

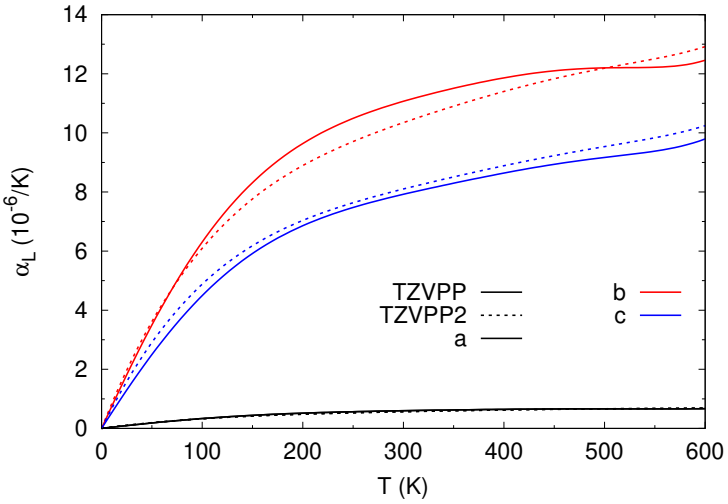

Figure S6: Linear thermal expansion coefficients of each lattice parameter as obtained for the 2x2x2 supercell with the TZVPP and TZVPP2 basis sets, respectively.

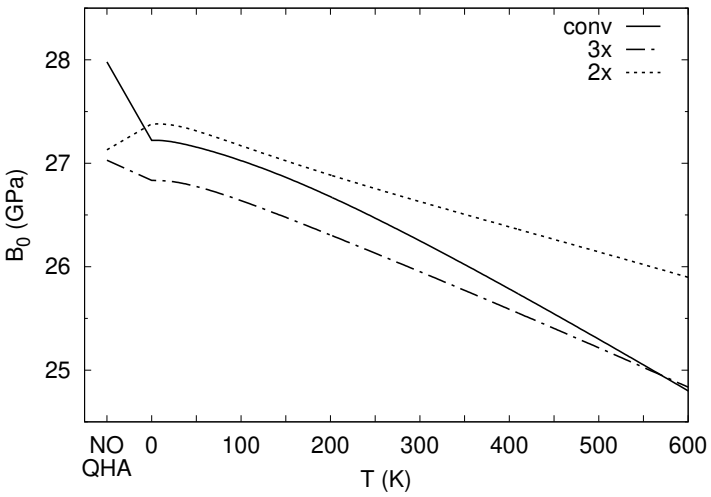

Figure S7: Bulk modulus as obtained with the TZVPP basis set for the 2x2x2, conv, and 3x3x3 supercells, respectively.

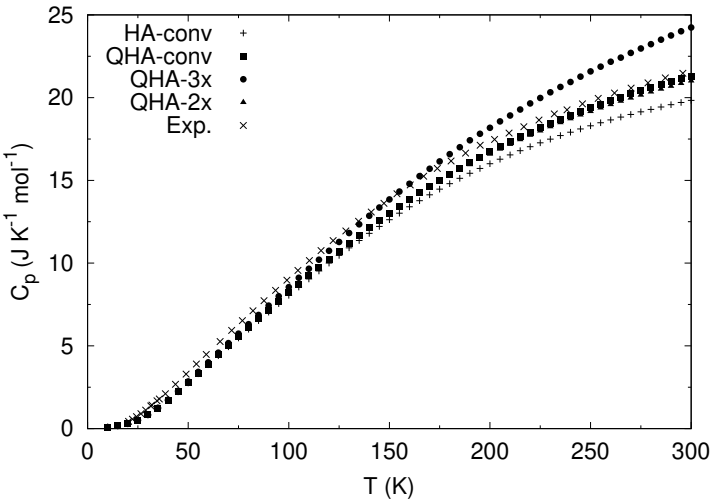

Figure S8: Heat capacity as obtained with the TZVPP basis set and QHA approach for the 2x2x2 (triangles), conv (squares), and 3x3x3 (circles) supercells, respectively. For comparison, the HA results for the conv supercell (pluses) and those reported experimentally by Stephenson et al. (crosses) in Ref. [12]