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Comment on "Polymorphism of boron phosphide: theoretical investigation and experimental assessment" by V. L. Solozhenko and S. F. Matar, *J. Mater. Chem. C*, 2022, **10, 3937**

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Crystal structure of rhombohedral boron phosphide recently predicted by DFT calculations was refined using experimental data of high-resolution transmission electron microscopy study.

In our paper¹ we reported stable crystal structure of previously unknown rhombohedral boron phosphide obtained using crystal chemistry rationale and unconstrained geometry optimization onto ground state structure by computations within density functional theory (DFT). Rhombohedral BP was found to belong to *R3m* space group, with unit-cell parameters $a = 3.217 \text{ \AA}$, $c = 7.866 \text{ \AA}$; and to be almost as cohesive as cubic boron phosphide.

Very recent high-resolution transmission electron microscopy study,² however, revealed that unit-cell parameters of experimentally observed rhombohedral BP are $a = 3.21 \text{ \AA}$ and $c = 23.58 \text{ \AA}$, i.e. *c*-parameter is triple. The new search for the ground state structure within DFT was carried out using plane-wave Vienna Ab initio Simulation Package (VASP) code with the projector augmented wave method for the atomic potentials (see Ref. 1 for details). The refined structure parameters of rhombohedral BP are presented in Table. One can see that the calculated unit-cell parameters are in excellent agreement with the experimental data.² Energy wise, the extended rhombohedral structure was found cohesive with magnitude $E_{\text{coh}} = -1.17 \text{ eV/atom}$ close to those of two other BP polymorphs.¹

Clearly, crystal structure predictions based on DFT calculations should be treated with caution, unless confirmed by experimental data.

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1. V. L. Solozhenko and S. F. Matar, Polymorphism of boron phosphide: theoretical investigation and experimental assessment, *J. Mater. Chem. C*, 2022, **10**, 3937-3943.

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2. B. A. Kulnitskiy, V. D. Blank, T. A. Gordeeva, V. A. Mukhanov and V. L. Solozhenko, TEM study of boron phosphide: Discovery of rhombohedral BP, *Solid State Commun.*, 2022, **354**, 114886.

Table Refined structure parameters of rhombohedral BP (in hexagonal setting)

Space group $R3m$ (No. 160). $a = 3.206 \text{ \AA}$, $c = 23.750 \text{ \AA}$

Atom	Wyckoff	x	y	z
B1	$3a$	0	0	0.004
B2	$3a$	0	0	0.227
B3	$3a$	0	0	0.449
P1	$3a$	0	0	0.088
P2	$3a$	0	0	0.310
P3	$3a$	0	0	0.544

$$d(\text{B-P}) = 1.96 \text{ \AA}$$

$$\angle\text{P-B-P} = 109.58^\circ$$