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Phosphorus Allotropes: Stability of Black versus Red Revisited with van der Waals Inclusive Density Functional Methods

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We evaluate the energetic stabilities of white, red and black allotropes of phosphorus using density functional theory (DFT) and hybrid functional methods, van der Waals (vdW) corrections (DFT+vdW and hybrid+vdW), vdW density functionals and random phase approximation (RPA). We find that stability of black phosphorus over red-V (i.e violet) is not ubiquitous among these methods, and the calculated enthalpies for the reaction $P(\text{red-V}) \rightarrow P(\text{black})$ are scattered between -20 and 40 meV/atom. With local density and generalized gradient approximations, and hybrid functionals, mean absolute errors (MAEs) in densities of P allotropes relative to experiments are found to be around 10%–25%, whereas with vdW-inclusive methods, MAEs in densities drop below $\sim 5\%$. While the inconsistency among the density functional methods could not shed light on the stability puzzle of black versus red P, comparison of their accuracy in predicting densities and the supplementary RPA results on relative stabilities indicate that opposite to the common belief, black and red-P are almost degenerate, or the red-V (violet) form of P might even be the ground state.

I. INTRODUCTION

Elemental phosphorus can exist in a variety of allotropic forms including white, red, black and their modifications,¹ and the interest in this rich chemistry has not diminished over the last century.^{2–11} Today, the exfoliated 2D form of black P, phosphorene, is emerging as a unique semiconducting material for electronic applications.^{12–15} The fundamental question of which form of elemental phosphorus is most stable at low temperatures and pressures has long been under debate, sparked by the discovery of black phosphorus under high pressures by Bridgman in the first half of the 20th century.^{2,3} This orthorhombic phase of P was found to be more stable at room temperature and pressure than red phosphorus on the basis of both vapor pressure and the relative heats of reaction with bromine as early as in 1914 and 1937.^{2,3} These findings were later criticized by Stephenson et al.⁴ based on the fact that the entropies calculated from any reasonable high-temperature extrapolation of the heat capacities measured up to room-temperature for red and black P could not reproduce the $P(\text{black}) \rightarrow P(\text{red})$ transformation observed at 820 K¹⁶ when the enthalpy of this transformation is taken from Jacobs,³ and therefore they reported that there was no conclusive evidence for the stability of black P over red under ambient conditions. Later, O’Hare et al.¹¹ used combustion calorimetry to show black P is more stable than red at low temperatures and pressures. The pressure-temperature phase diagram by Brazhkin and Zerr¹⁰ also supports this finding, but their results were limited to qualitatively showing the existence of a stability region for red P at low pressures and at temperatures higher than stability region of the black form. However, in all such calorimetric experiments, fully isolating a single and uncontaminated form of P is known to be a major challenge limiting the accuracy of measurements.^{1,4,17} Today, black P is therefore accepted as *probably* the most

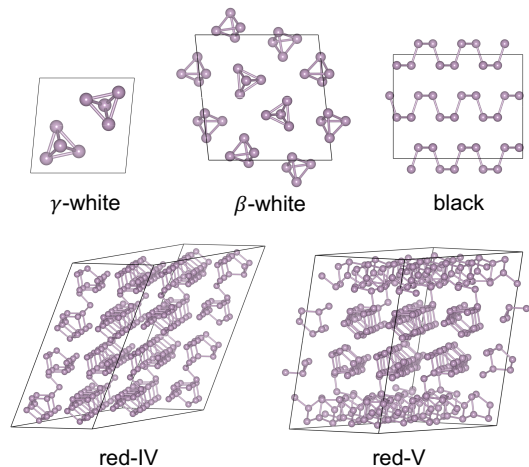


FIG. 1. Crystal structures of γ -white, β -white, red-IV, red-V and black phosphorus.

stable phase at room temperature and pressure.^{4,18}

Allotropes of P with known crystal structures reported in the Inorganic Crystal Structure Database (ICSD)¹⁹ are shown in Fig. 1 with details listed in Table I. The most common form and the reference state of P is white P. The room temperature reference state α -white is a crystal of P_4 molecules arranged similar to the α -Mn structure, but the orientational disorder of these molecules has not allowed a successful structure refinement.⁹ The low temperature β and γ forms of white P have resolved crystal structures where P_4 tetrahedra occupy γ -Pu (bcc-like) and distorted-bcc like lattices, respectively.^{8,9} β -white is often accepted as the low temperature reference state for P.²⁰ Red P can be synthesized in many modifications numbered from I to V,¹ where only IV and V are known to exist in crystalline form.⁴ Violet phosphorus, also known as Hittorf’s phosphorus, is a monoclinic crystal comprised of linked pentagonal tubes of P. Recently

TABLE I. Allotropes of phosphorus with well-characterized crystal structures available in the ICSD.¹⁹ Z is the number of atoms in the primitive cell.

P allotrope	Space group	Z	ICSD No.	Other names
Red-IV	$P\bar{1}$	42	391323	Fibrous red
Red-V	$P2/c$	84	29273	Hittorf's, Violet
Black	$Cmca$	4	23836	
γ -white	$C2/m$	8	154318	
β -white	$P\bar{1}$	24	68326	

Ruck et al.⁷ showed that the crystal structure of violet P can be ascribed to what is historically known as the red-V form, whereas the fibrous-red crystal structure is identical to the red-IV form of P.

The relative stabilities of red, black and white allotropes from different assessments of experimental thermodynamic data are listed in Table II, with respect to the white-P reference state as traditionally reported. Despite the quantitative agreement of red-V P being about ~ 180 meV/atom more stable than white P, the discrepancies between data reported for black P cast doubt on the reliability of the experimental measurements, which, in fact are prone to numerous difficulties.¹ The purity and crystallinity of red and black phosphorus in experiments are often questionable, vaporization kinetics are sluggish, and red phosphorus has five variants that further complicate the calorimetric measurements.^{1,4,17}

Density functional theory (DFT) analysis of the relative stabilities of P allotropes showed that the standard generalized gradient approximation (GGA)²¹ fails to reproduce the commonly accepted stability of black P over red P,²² and inclusion of one type of dispersion correction in DFT was suggested to correct this disagreement.^{23,24} On the other hand, there has been a remarkable progress in development of a wide spectrum of new, and more accurate van der Waals (vdW) inclusive DFT methods in recent years,²⁵⁻³² and whether the stability of black P over red P is a universal result among these functionals is not known. In this work, we carry out a comprehensive analysis of what (semi)-local density functionals, and the wide range of recently developed vdW functionals and dispersion correction methods predict for the relative stabilities of the phosphorus allotropes. We find that the vdW-inclusive DFT methods, in fact, yield inconsistent predictions for the relative stabilities of black and red forms; however, on the basis of a concurrent analysis of the accuracy of these methods in predicting densities of the allotropes and the results from random phase approximation (RPA) calculations, we show that red and black P are either degenerate, or red-V phosphorus can be the actual ground state.

II. METHODS

We used the Vienna Ab-initio Simulation Package (VASP)³³⁻³⁶ in all first-principles calculations. The projector augmented wave potential for P was used with s^2 and p^3 electrons treated as valence.³⁷ For the local density approximation (LDA) functional, we used the parameterization by Perdew and Zunger.³⁸ For the GGA functional we used the Perdew-Burke-Ernzerhof (PBE) formulation.^{21,39} For hybrid calculations, we used the Heyd-Scuseria-Ernzerhof (HSE06) functional.^{40,41} We used the D2, D3 (with zero-damping) and D3/BJ (i.e., with Becke-Johnson damping) methods by Grimme and co-workers.²⁵⁻²⁷ The local environment dependent approach by Tkatchenko and Scheffler (TS)²⁸⁻³⁰ was employed to add the long range dispersion energy corrections to PBE and HSE06 functionals. We used the ‘‘optimized’’ vdW-density functionals optB86b and optB88 by Klimes,^{31,32} which are based on the vdW-density functional proposed by Dion et al.⁴² A plane-wave kinetic energy cutoff of 520 eV was used in all calculations.

Initial geometries (i.e. before relaxation) of all crystal structures were obtained from the experimental structures reported in the Inorganic Crystal Structure Database (ICSD),¹⁹ with the corresponding ICSD numbers listed in Table I. For each phosphorus structure considered, we performed multistage relaxations of all degrees of freedom and evaluated the total energy in a final static run using all different functionals and vdW-inclusive methods above. We used Γ -centered k-point grids of at least 2,000 k-points per reciprocal atom for static calculations, while relaxations were performed at approximately half of the corresponding k-point densities. In HSE calculations, the Hartree-Fock kernel was evaluated on a k-point grid reduced by a factor of two. RPA calculations were performed at experimental lattice parameters for all allotropes. The exact exchange contribution to the RPA total energy was calculated at the k-point density described above. However, due to its computational expense (and faster convergence with number of k-points^{43,44}), the RPA correlation itself was calculated at approximately 20%-25% of that k-point density.

Phonon calculations were performed using phonopy,⁴⁵ with the frozen phonons method. In phonon calculations, we used $2 \times 2 \times 2$ supercells, i.e. 32 atom-cell for black and 336 atom-cell for red-V phosphorus, with k-point meshes of $9 \times 6 \times 5$ and $1 \times 1 \times 1$ (Γ -point only), respectively. Structures were initially relaxed until residual forces were less than 1×10^{-5} eV/Å. Displacement forces were calculated with an electronic convergence criterion of 1×10^{-9} eV/cell. Structures were visualized using VESTA.⁴⁶

III. RESULTS AND DISCUSSION

In Figure 2a, we show the energetic stabilities (relative to the low temperature reference state β -white) of crystalline allotropes of P listed in Table I calcu-

TABLE II. Reported experimental enthalpies of red and black allotropes of P relative to α -white for 298 K data or β -white for 0 K data, obtained from JANAF²⁰ and National Bureau of Standards (NBS)⁴⁷ thermochemical tables, and other cited reference. All energies are in units of meV/atom. The relatively large energy difference between red and black polymorphs in Ref.3 is believed to be due to presence of a higher energy form of red P, possibly red-IV.⁴

P allotrope	JANAF 0 K	JANAF 298 K	NBS 298 K	Ref. 3 ^a	Ref. 11	Ref. 1
Red-V (Red-IV)	-163 (-111)	-181 (-129)	-182	[-181]	-186	-182
Black	-116	-133	-407	[-362]	-220	-
α -white/ β -white	0	0	0	0	0	0

^aJacobs reported only the enthalpy difference for the reaction P(red) \rightarrow P(black); therefore, for consistency, we used JANAF 298 K enthalpy for red-V to change the reference state of black P to white P in this column.

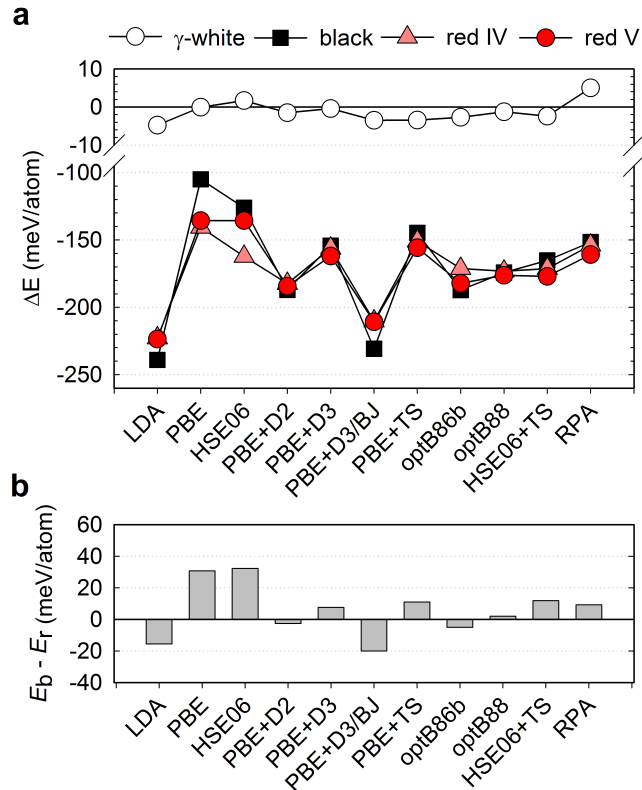


FIG. 2. (a) Energetic stabilities of γ -white, black, red-IV and red-V allotropes of phosphorus relative to β -white phosphorus calculated with different density functional, hybrid and vdW-inclusive methods. (b) Relative stabilities of black and red-V forms with calculated with different methods.

lated with the common (semi)-local functionals and vdW-inclusive methods including LDA, GGA-PBE, hybrid HSE06, five vdW-dispersion corrected methods, and two vdW-functionals, as well as with the nonlocal RPA (which, by construction yields accurate correlation including long-range dispersion effects). The γ -white form is found to be slightly more stable than (or nearly degenerate with) β -white P by all methods, in agreement with the observed phase transformations in experiments.⁸ Red-V is accepted as the most stable form of red P,^{1,20} and the experimental enthalpy difference between red-

IV and V in Table II is around 50 meV/atom. We find that red-V is also lower in energy than red-IV P for all methods except PBE and HSE06. However, the energy differences between red-IV and red-V P in Figure 2 are an order of magnitude smaller than the experimental values. Given the fact that red-IV and red-V bear a high structural resemblance, we believe the computations hint at an overestimation of the enthalpy difference in experiments, possibly due to imperfect crystallinity of red-IV samples.^{1,7}

A more intricate problem is the stability of black P over red-V (violet) P, where we find that vdW methods all give different trends as shown in Figure 2b. Such inconsistencies in stability predictions of polymorphs among different vdW-inclusive methods were actually observed for other materials as well.⁴⁸ Here the energies calculated with various DFT approaches for P(red-V) \rightarrow P(black) cover a wide range of values between -20 and 40 meV/atom. LDA, PBE+D2, PBE+D3/BJ, and optB86b predict that black P is more stable than red-V P. In contrast, PBE, HSE06, PBE+D3, PBE+TS, optB88, and HSE06+TS predict that red-V P is more stable than black P, which are consistent with the higher-level RPA calculations. For the vdW-inclusive methods, it is puzzling that calculations with similar levels of theory, such as similar dispersion correction methods or similar vdW density functionals (vdW-DFs), give opposite predictions for the stability of black vs. red-V P. The magnitude of the energy difference between black and red-V P, however, is smaller in most of the vdW-inclusive methods compared to LDA, PBE and HSE06 or the experimental enthalpies in Table II. Our current results also indicate that the recent conclusion by Bachhuber et al.²³ where they suggested vdW interactions included via PBE+D2 stabilize black P over other allotropes, in fact, does not generalize to other more advanced dispersion correction or opt-type vdW-DF methods, or to RPA as evident from Figure 2.

Given the relatively small energy difference between black and red-V P predicted by the vdW-inclusive methods, we should evaluate whether temperature has any considerable effect on the relative stabilities of these two forms of P. Stephenson et al.⁴ measured the heat capacities of black and red forms from ~ 15 K to room temperature. Their results indicate that the difference between

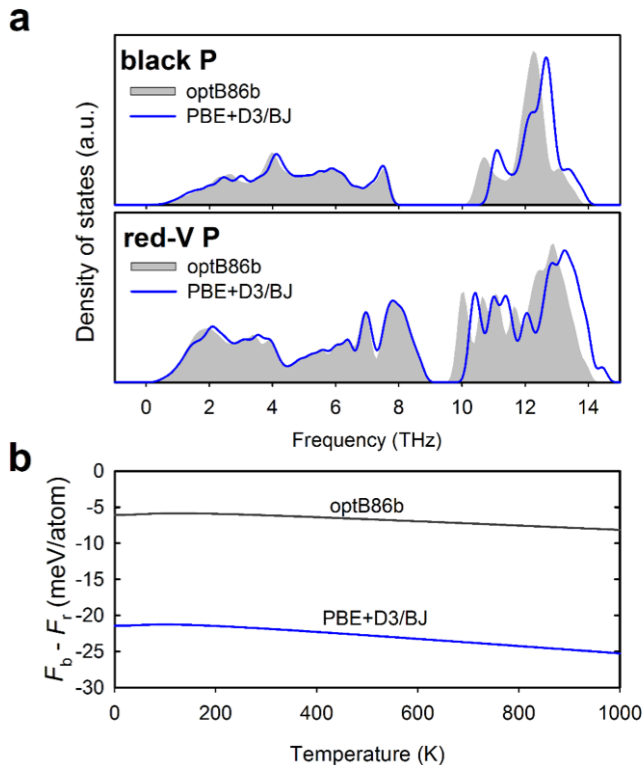


FIG. 3. (a) Phonon density of states of black and red-V P calculated using optB86b and PBE+D3/BJ, (b) and the corresponding free energy differences ($F_b - F_r$) as a function of temperature.

zero K and room temperature enthalpy of the reaction $P(\text{red-V}) \rightarrow P(\text{black})$ is only a fraction of an meV. The experimental room-temperature entropies for black and red-V P are also very similar at 22.59 and 22.85 J/mol-K, respectively.^{4,20} Using these experimental measurements, we estimate the difference between 0 K and 298 K value of the Gibbs free energy of the reaction $P(\text{red-V}) \rightarrow P(\text{black})$ as only 1 meV/atom at standard pressure. The corresponding value obtained from the phonon calculations performed using optB86b and PBE+D3/BJ (Figure 3), representing the two distinct domains of vdW-inclusion methods (i.e. functionals and dispersion corrections) are also only 1 and 2 meV/atom, respectively, and therefore agree well with the value from the experimental heat capacity measurements. Furthermore, the zero-point vibrational energies (ZPEs) of red and black P calculated from the phonon spectra in Figure 3 are almost identical at around 50 meV/atom for both vdW-inclusive methods tested; i.e., ZPEs do not have a considerable effect on the energy of $P(\text{red-V}) \rightarrow P(\text{black})$ either. Therefore the temperature and the zero-point vibrational effects on the relative stability of red-V vs. black P are negligible and the ground-state energy difference should itself adequately represent this relative stability up to moderate temperatures. However, there apparently is no con-

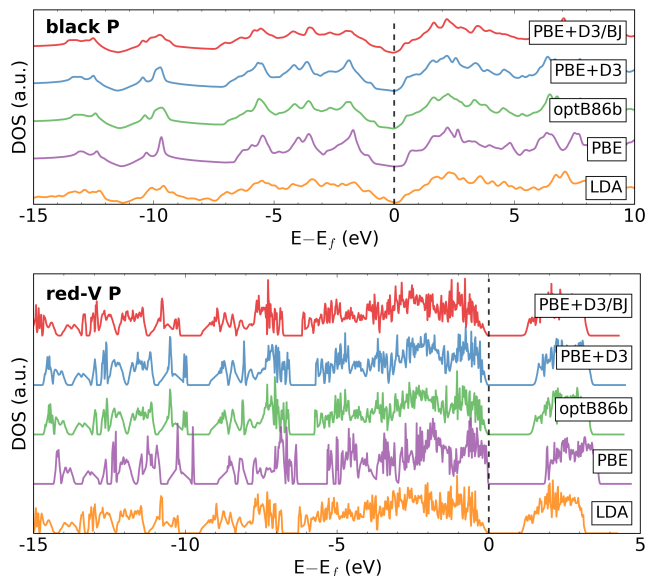


FIG. 4. Electronic density of states (DOS) of black (top) and red-V (bottom) phosphorus calculated with LDA, PBE, optB86b, PBE+D3 and PBE+D3/BJ. E_f denotes the Fermi level.

sensus on the ground state stability of black vs. red-V P among the state-of-the-art vdW-inclusive DFT-based methods tested in this work. We should mention that in contrast to historical suggestions of black transforming to red around 820 K in the 1930s,¹⁶ our phonon calculations indicate the stability of black over red in fact slightly increases with increasing temperature, suggesting that high temperature thermodynamic properties of these allotropes should be investigated carefully in future experiments.

To understand the source of the discrepancy in relative stabilities of black and red-V P in (semi)-local and vdW-inclusive methods, we further compare their electronic density of states (DOS) calculated with a representative set of such methods in Figure 4. For black P, we find that all methods result in a similar DOS, whereas for red-V, calculated energy levels in occupied states show more variation. For example, PBE yields highly localized low energy states in red-V, likely contributing significantly to its stabilization of red-V over black P. Compared to PBE, LDA does not yield such localized low energy states in red-V, which is consistent with LDA stabilizing black over red-V P. Having also a GGA basis, the optB86b and PBE+D3 methods (which represent two different classes of vdW-inclusive methods) also show well-localized low-energy states for red-V, similar to PBE. Therefore, for these methods, inclusion of vdW-interactions energetically favors the layered form of black P over the tubular form of red-V and counter-balances “over-stabilization” of red-V by standard PBE. The resulting interplay between electronic and vdW contributions brings the energy difference between red-V and black P down to a few

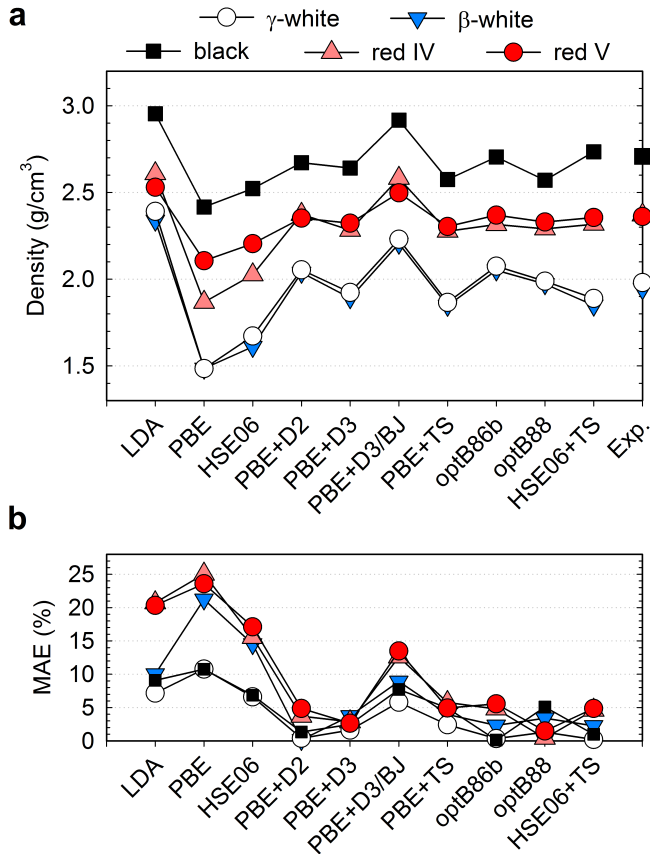


FIG. 5. (a) Densities of γ -white, β -white, red-IV, red-V and black allotropes of phosphorus relative calculated with different density functional, hybrid and vdW-inclusive methods, and (b) corresponding mean absolute errors. Experimental densities are based on the ICSD crystal structures. Experimental densities of red-IV and red-V are very similar and overlap in the plot.

meV per atom as observed in Figure 2. Interestingly, despite being PBE based, PBE+D3/BJ method also yields an electronic structure similar to LDA for red-V, and in turn energetically favors black over red-V as LDA does. Besides the resulting electronic structures, another common point between LDA and PBE+D3/BJ is that they both underestimate the volumes of allotropes compared to other methods, and therefore, next, we investigate the variation in mass densities of allotropes among different DFT techniques.

The densities of allotropes of P calculated with the common (semi)-local functionals and vdW-inclusive methods are shown in Figure 5a along with the mean absolute errors (MAE) in the calculated densities with respect to experimental data in Figure 5b. The experimental order of densities (black > red-V \approx red-IV > γ -white > β white) is captured with all methods, but LDA, PBE and HSE predictions have very large MAEs

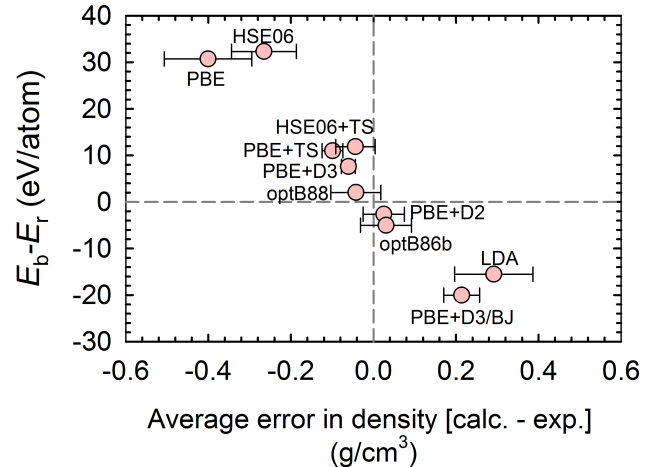


FIG. 6. Energy difference between black and red-V P ($E_b - E_r$) plotted against average error made by a given density functional in predicting densities of all five P allotropes considered (i.e. β -white, γ -white, black, red-IV and red-V). Error-bars show the standard deviations in these errors.

ranging from 5 to 25%. All vdW-inclusive methods bring the errors down to less than $\sim 5\%$ (except D3/BJ).

LDA is well-known to overbind atoms at short distances,⁴⁹ which is likely one of the reasons why it stabilizes black over red-V P as the former has a much higher density. PBE and HSE do not overbind as in the LDA, but they still lack the non-local correlation that leads to vdW interactions which is one of the major contributions to the binding of molecular P solids. Lacking this binding, opposite to LDA, PBE and HSE seem to considerably underestimate densities, and at the same time stabilize the lower density red-V form over the black form. In fact, as shown in Figure 6, there is a clear correlation between the predicted densities in Figure 5a and the relative stabilities of phases in Figure 2a and 2b; i.e. methods that predict higher densities compared to experiments (i.e. those with an overbinding tendency) systematically yield more negative energies for denser phases, and vice versa. Although it is an improved version of the D3,²⁵ PBE+D3/BJ significantly overestimates the densities of all P allotropes on a level comparable to LDA, which hints at an overbinding tendency at short-distances for PBE+D3/BJ in solids of P. Only two other vdW-inclusive methods predict negative enthalpies for P(red-V) \rightarrow P(black). These enthalpies are only -5 meV/atom (for optB86b) and -3 meV/atom for (PBE+D2), with the rest of the vdW-inclusive methods giving positive values in Figure 2b. These results are counter-intuitive as they contradict the common belief that black is the most stable allotrope, and show it is possible that black and red-V forms of P are almost degenerate, or that red-V might even be the thermodynamic ground state.

Finally, we should emphasize that as shown in case

of the relative stabilities of P allotropes, despite the recent progress in the area of developing new vdW-inclusive DFT methods, validity or applicability of some of these methods, including vdW-DFs or dispersion correction methods, should still be tested carefully, at least in thermochemical studies, before arriving at major conclusions. Where reliable experimental thermochemical data is lacking, more readily available volumetric mass density data can be used as a preliminary benchmark set to gauge the overall performance of the vdW-inclusive methods, as we showed for the case of P allotropes in Figure 5.

IV. CONCLUSION

Black P is widely accepted as the most stable form of phosphorus at low temperatures and pressures. However, evaluating the relative stabilities of P allotropes using the current state-of-the-art vdW-inclusive DFT methods, and in particular the black P versus red-V P (also known as violet P), we found that: (i) the energy difference between black and red P is likely to be an order of magnitude smaller than the available (and contradictory) experimental data, and (ii) black P is not the ubiquitous ground state structure among the vdW-inclusive methods. In fact, with a concurrent analysis of the densities

of allotropes, we found that there exists a strong correlation between the over-binding tendencies of the density functional methods and the energetic stability of black P versus red-V P. On the basis of this comparison with the accuracy of the vdW-DFT in predicting densities, we conclude that black P and red-V are either degenerate, or red-V can in fact be the ground state structure of the elemental phosphorus. This conclusion is further supported by the random phase approximation calculations of relative stability of black and red-V phosphorus. Further thermodynamic experiments are essential to shed light on the stability of black P over red P, and also to assess the accuracy of vdW-inclusive DFT methods in predicting this stability.

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