research papers

A new polymorph of white phosphorus at ambient conditions

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Phosphorus exists in several different allotropes: white, red, violet and black. For industrial and academic applications, white phosphorus is the most important. So far, three polymorphs of white phosphorus, all consisting of P_4 tetrahedra, have been described. Among these, β-P_4 crystallizes in the space group $P\bar{1}$ and γ-P_4 in the space group $C2/m$. α-P_4 forms soft plastic crystals with a proposed structure in the cubic space group $I\bar{4}3m$ with the lattice constant $a = 18.51\,(3)$ Å, consisting of 58 rotationally disordered tetrahedra and thus is similar to the structure of α-Mn. Here we present a new polymorph, δ-P_4. It crystallizes as a sixfold twin with the cell dimensions $a = 18.302\,(2)$, $b = 18.302\,(2)$, $c = 36.441\,(3)$ Å in the space group $P2_12_12_1$ with 29 P_4 tetrahedra in the asymmetric unit. The arrangement resembles the structure of α-Mn, but δ-P_4 differs from α-P_4. DFT calculations show δ-P_4 to be metastable at a similar energy level to that of γ-P_4.

1. Introduction

Phosphorus exists in several different modifications: white, red, violet and black (Fig. 1). Its affinity for oxygen is high, so it exists in nature mainly as phosphates, containing the PO_4^{3-} anion. This is difficult to activate chemically in contrast to white phosphorus P_4, which spontaneously ignites when exposed to air. This makes the element a versatile reagent in organophosphorus chemistry (Iaroshenko, 2019; Donath *et al.*, 2022; Grützmacher, 2022).

The different modifications of phosphorus vary markedly in their physical properties and chemical reactivity. The most stable modification at room temperature is polymeric black phosphorus P_n. This polymorph has semiconducting properties. It displays a layered structure consisting of anellated chair-shaped six-membered rings (Fig. 1, left). At ambient pressure it crystallizes in the space group $Cmca$ with $a = 3.31$, $b = 10.50$ and $c = 4.38$ Å (Hultgren *et al.*, 1935; Brown & Rundqvist, 1965). Under increasing pressure, it undergoes several phase transitions (Jamieson, 1963; Kikegawa & Iwasaki, 1983; Kikegawa *et al.*, 1987; Scelta *et al.*, 2017; Marqués *et al.*, 2008; Akahama *et al.*, 1999; Sugimoto *et al.*, 2012); for example, at room temperature the first phase transition at ∼5 GPa leads to the space group $R\bar{3}m$ with $a = 3.38$ and $c = 8.81$ Å. Fibrous red phosphorus crystallizes in the space group $P\bar{1}$ with $a = 12.198$, $b = 12.986$, $c = 7.075$ Å, and $\alpha = 116.99$, $\beta = 106.31$, $\gamma = 97.91°$ (Fig. 1, right) (Ruck *et al.*, 2005). It consists of tubes with pentagonal cross-sections. The tubes are built from cages of eight or nine phosphorus atoms
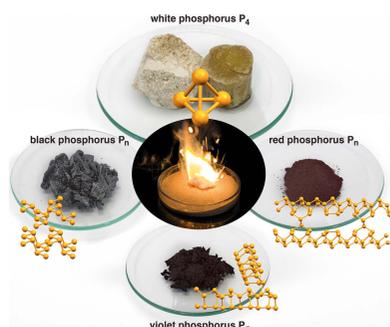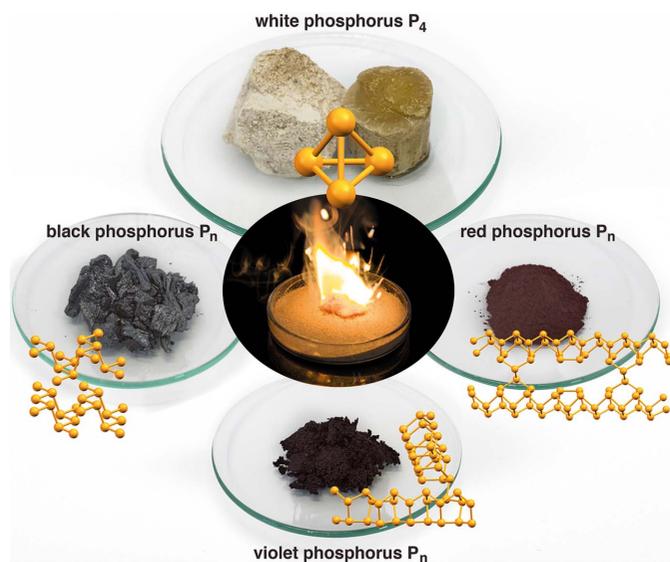
Figure 1
Known modifications of elemental phosphorus under ambient conditions: their macroscopic manifestations combined with the structures at the atomic level.

connected by dumbbells of two phosphorus atoms, and interconnect to form a double tube. This is similar to the structure of violet or Hittorf's phosphorus, which crystallizes in the space group $P2/c$ with $a = 9.21$, $b = 9.15$, $c = 22.60$ Å and $\beta = 106.1°$ (Fig. 1, bottom) (Thurn & Krebs, 1969; Zhang *et al.*, 2020). Zhang *et al.* (2020) stated that their structure differs slightly from the structure described by Thurn & Krebs (1969) and discussed the differences [*e.g.* different space groups ($P2/n$ and $P2/c$), c axes and ß angles]; however, both structures can be transformed into each other by the matrix $-100\ 0-10\ 101$, hence there is no difference between them but they are identical.

Recently, another structure has been described (Cicirello *et al.*, 2023) in the space group $C2/c$ with eleven phosphorus atoms in the asymmetric unit.[1] The red and violet P_n structures differ only in the orientation of the two tubes relative to each other: they are perpendicular to each other in the violet modification and parallel in the red polymorph. Although white phosphorus is the most toxic and reactive modification, it is a major source for industrial and academic applications (Donath *et al.*, 2022). To date, three modifications of white phosphorus have been described in the literature (Simon *et al.*, 1997). Though the structures for β-P_4 (Simon *et al.*, 1987) and γ-P_4 (Okudera *et al.*, 2005) are unequivocal, no structural data are available for α-P_4. γ-P_4 is the stable low-temperature form

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[1] The cell parameters are nearly identical to the structure refined in $P2/n$ with P_{21} in the asymmetric unit by Zhang *et al.* (2020) and hence to Thurn & Krebs (1969). The data quality of Cicirello *et al.* (2023) is very poor. In the Checkcif report there are several A alerts, *e.g.* no anisotropic refinement, max residual density of 4.65 e Å^{-3}, $wR2 = 0.49$. It is possible to refine the coordinates of the structure deposited by Zhang *et al.* (2020) against the data deposited by Cicirello *et al.* (2023). Of course, half of the data are then missing and 5 of the 21 P atoms adopt negative U_{iso} values. However, $wR2$ reaches 0.29 and the highest residual density is 2.09 e Å^{-3}. Therefore, there is reasonable doubt whether this is really a new structure and whether P_{11} is indeed the content of the asymmetric unit, rather than P_{21} as in the original structure by Thurn & Krebs (1969).

and crystallizes in the space group $C2/m$ with $a = 9.1709$ (5), $b = 8.3385$ (5), $c = 5.4336$ (2) Å and $\beta = 90.311$ (3)° with four formula units per cell ($Z = 4$) (Okudera *et al.*, 2005). It transforms into the intermediate modification β-P_4, which crystallizes in the space group $P\bar{1}$ with $a = 5.4788$ (5), $b = 10.7862$ (11), $c = 10.9616$ (11) Å, $\alpha = 94.285$ (8), $\beta = 99.653$ (7), $\gamma = 100.680$ (7)° and $Z = 6$ (Simon *et al.*, 1987). The room-temperature form α-P_4 has been described as a plastic crystal (Simon *et al.*, 1997). As early as 1930, a powder photograph taken at $-35°$C was interpreted in terms of a cubic cell with $a = 7.17$ Å (Natta & Passerini, 1930). However, this key structure – 'a riddle, wrapped in a mystery, inside an enigma' – remained unsolved. In 1952 single-crystal data were collected in the cubic system with $a = 18.51$ (3) Å, assuming the space group $I\bar{4}3m$, but the structure was never solved, which was attributed to rotational disorder (Corbridge & Lowe, 1952). As the most reasonable approximation, it was assumed that the centroids of the P_4 tetrahedra are arranged similar to the atomic positions of the 58 Mn atoms in the complicated structure of α-Mn (von Schnering, 1981). The most recent verdict is that crystallographic investigations are hampered by a partial transition to red phosphorus or that a high degree of thermal motion precludes a structure determination (Simon *et al.*, 1997).

2. Experimental

In the course of a synthesis involving the activation of white phosphorus, we discovered a new polymorph of phosphorus P_4, which we introduce in this publication as δ-P_4. Diffraction data were collected from an apparently cubic crystal with $a = 36$ Å at 100 K. We assumed at first that the data corresponded to the proposed reaction product, not the starting material. The diffraction pattern indicated twinning. Fig. 2(a) shows every second reflection to be missing in every second line. This can be interpreted as a threefold twin, and all reflections can be indexed with three different orientations and cell constants of approximately $a = 18.3$, $b = 18.3$, $c = 36.5$ Å and $\alpha = \beta = \gamma = 90°$ [Figs. 2(b)–2(d)]. These cell constants suggest a tetragonal space group. However, the data derived by integration with these three orientation matrices, with subsequent detwinning assuming $4/m$ symmetry, showed only orthorhombic symmetry and hinted at additional twinning that mimicks tetragonal symmetry. This means that there are six twin domains, because each of the three domains has an additional domain, generated by reducing the crystallographic fourfold symmetry to twofold symmetry.

Consequently, the integration was repeated, now using six orientation matrices. The matrices of the twin laws are given in the supporting information. After detwinning, the space group could be determined unequivocally to be $P2_12_12_1$. The structure could be solved in this space group (Sheldrick, 2008) and refined as a sixfold twin without any disorder (Sheldrick, 2015b; Sevvana *et al.*, 2019). The refinement converged to $R1$ [$I > 2\sigma(I)$] = 0.0363. More details can be found in the supporting information.

With these results in hand, we attempted to find suitable crystallization conditions for this new polymorph. The first trials using CS_2 as the solvent led to soft plastic crystals, as already described in the literature as α-P_4. They diffracted weakly to a resolution of *ca* 1.6 Å. The cell constants suggested cubic symmetry with a = 18.7 Å and the structure could not be solved. Crystallization from dry, degassed hexane gave colourless block-shaped single crystals (see Fig. 3) which were identified as the δ-polymorph we had just investigated. The crystals were again twinned, and of the same quality as before, leading to the same ordered structure with similar quality indicators (see Table S1 of the supporting information).
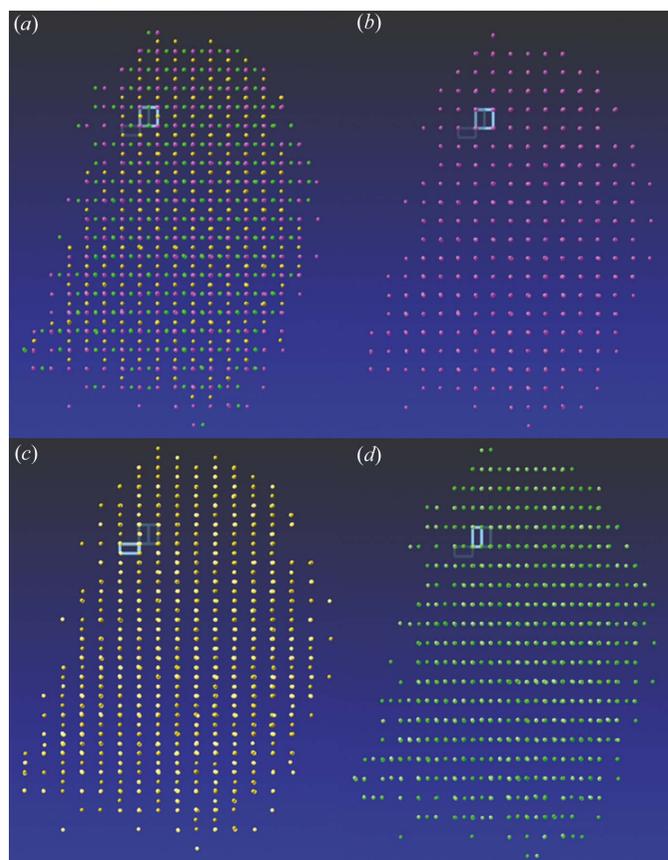
3. Results

In the literature, the α-P_4 polymorph is described as a cubic structure with a = 18.51 (3) Å in the most probable space group $I\bar{4}3m$. The similarity to α-Mn was mentioned (von Schnering, 1981). In our δ-P_4 structure, one axis is doubled and the others are slightly shorter compared with these observations. However, the arrangement of the P_4 tetrahedra indeed resembles the structure of α-Mn, which crystallizes in space group $I\bar{4}3m$ (see Fig. 4) (Oberteuffer & Ibers, 1970). The cubic symmetry forces the packing to be identical along all three axes (Fig. 4, left), whereas they are very similar in the new orthorhombic δ-P_4 modification (Fig. 4, right). This can be visualized using the centroids of the δ-P_4 tetrahedra (Fig. 4, centre).

The asymmetric unit consists of 29 P_4 tetrahedra. A Z' value as high as 29 might lead one to think of modulation. However, the typical signs of modulation (strong central reflections with weaker satellites) were absent from the diffraction pattern. Additionally, we note the similarity to the non-modulated structure of α-Mn with similar environments of the Mn atoms and the P_4 tetrahedra. In α-Mn there are four independent Mn atoms with different crystallographic symmetry and environments (Types I–IV) corresponding to 58 atoms in the unit cell.

Figure 2
Plot of the Bragg reflections used for indexing (Bruker, 2016). (*a*) All reflections, (*b*) first, (*c*) second and (*d*) third domain. The light pale rectangles indicate the corresponding cell.

Figure 3
Crystals of the new polymorph.
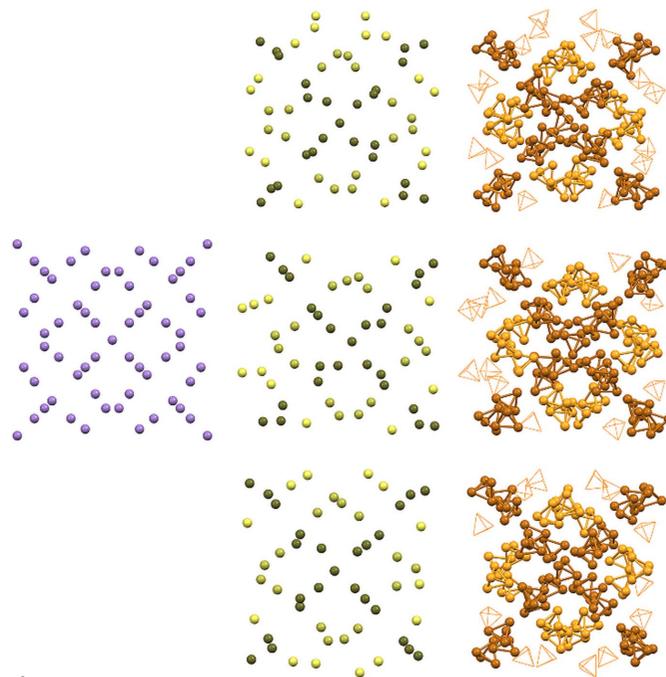
Figure 4
Packing of α-Mn compared with δ-P_4: left: α-Mn along the *a* axis, which is identical to the *b* and *c* axes caused by the cubic symmetry. Centre: centroids of the P_4 tetrahedra along the *a* axis (top), *b* axis (middle) and *c* axis (bottom). Right: full tetrahedra of the new δ-P_4 polymorph along the *a* axis (top), *b* axis (middle) and *c* axis (bottom).

Two belong to Type I [Fig. 5(*a*)], eight to Type II [Fig. 5(*b*)], 24 to Type III [Fig. 5(*c*)] and 24 to Type IV [Fig. 5(*d*)]. Similar environments can be observed for the P_4 units of the δ-P_4 structure: thus there is one tetrahedron of Type I [Fig. 5(*e*)], four of Type II [Fig. 5(*f*)], 12 of Type III [Fig. 5(*g*)] and 12 of Type IV [Fig. 5(*h*)], exactly half as many of each type as for α-Mn, coordinated in the same way as in α-Mn (see Figs. 5 and 6 and the supporting information). Therefore, our new δ-P_4 polymorph indeed resembles α-Mn, as commented by von Schnering (1981), but it is definitely different from the α-P_4 form discussed in previous publications (Simon *et al.*, 1997, 1987; Corbridge & Lowe, 1952).

The P_4 tetrahedra of Types I [Fig. 6(*c*)] and II [Fig. 6(*d*)] are surrounded by 16 further tetrahedra, and the resulting global polyhedron can be described as a distorted and truncated tetrahedron [Fig. 6(*a*)] with 4 tetrahedra above the sixfold planes [Fig. 6(*b*)]. The distortion is higher for Type II. The tetrahedra of Type IV [Fig. 6(*h*)] are coordinated by 12 further

tetrahedra, leading to a distorted icosahedron [Fig. 6(*g*)], whereas the polyhedron of the Type III tetrahedra [Fig. 6(*f*)], with coordination number 13, can be described as a hexagonal antiprism with one corner missing and capped by two tetrahedra above and below [Fig. 6(*e*)].

Our new polymorph δ-P_4 and the old α-P_4 are correlated in the following way: in both the P_4-tetrahedra probably show an overall structural pattern reminiscent of α-Mn, provided that only the centroids of the tetrahedra are taken into account. Compared with α-P_4, in the new δ-P_4 polymorph all 29 tetrahedra in the asymmetric unit are ordered (rather than disordered), one cell axis is doubled, the cell is primitive and not I-centred, and the symmetry is reduced from cubic to orthorhombic. None of the tetrahedra are related by translational or rotational symmetry. In α-Mn and presumably also in α-P_4 there are only 29/24 atoms or tetrahedra, respectively, in the asymmetric unit. Therefore, severe rotational P_4-disorder is introduced, permitting only low-resolution diffraction data for
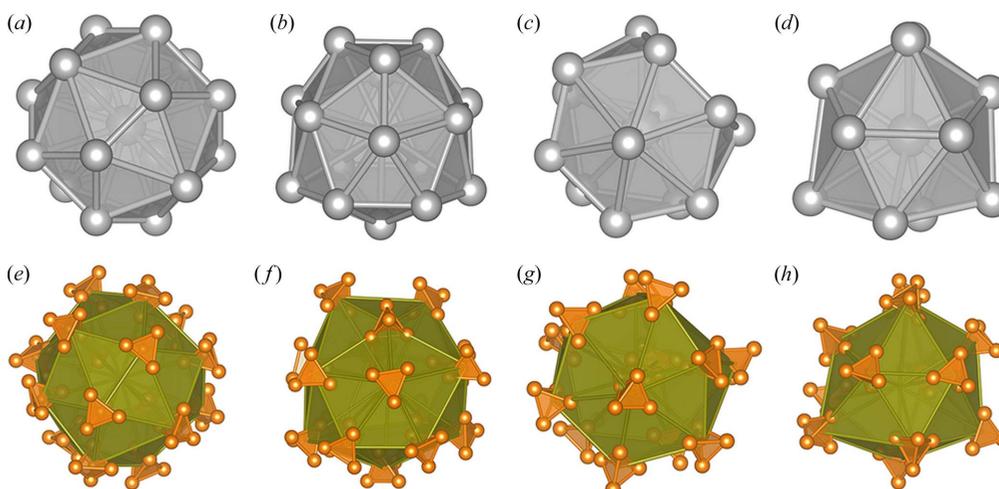
Figure 5
(*a*)–(*d*) Comparison of the α-Mn polyhedra (Momma & Izumi, 2011) and (*e*)–(*h*) the environment types of the new δ-P_4 modification. (*a*) α-Mn Type I, (*b*) α-Mn Type II, (*c*) α-Mn Type III and (*d*) α-Mn Type IV, (*e*) δ-P_4 Type I, (*f*) δ-P_4 Type II, (*g*) δ-P_4 Type III and (*h*) δ-P_4 Type IV.
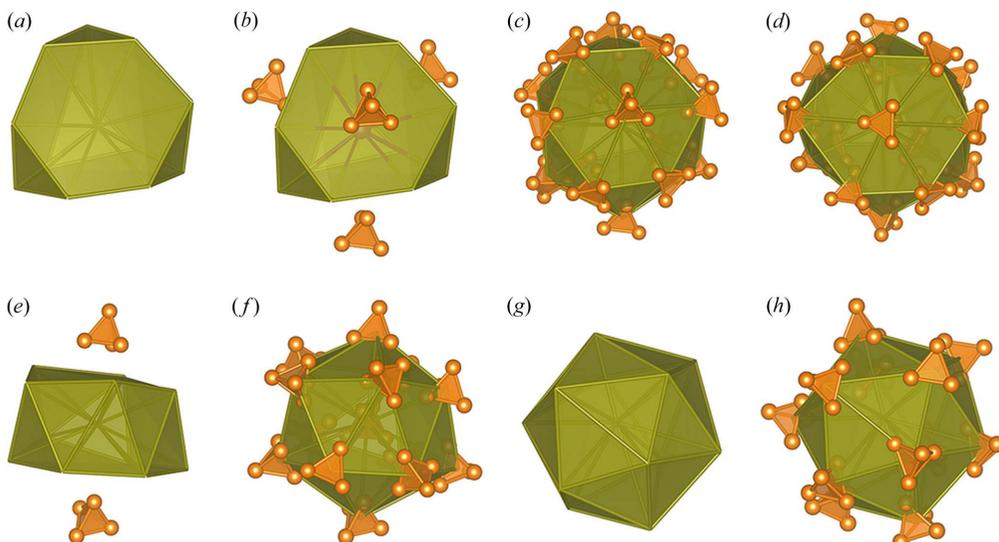
Figure 6
Polyhedra of the four environment types: (*a*) truncated tetrahedron, (*b*) truncated tetrahedron with the hexagonal planes capped by P_4 tetrahedra, (*c*) all P_4 tetrahedra of Type I, (*d*) all tetrahedra of Type II, (*e*) hexagonal antiprism with one edge missing of Type III and the hexagonal planes capped by P_4 tetrahedra, (*f*) all P_4 tetrahedra of Type III, (*g*) icosahedron, (*h*) icosahedron of Type IV with all P_4 tetrahedra (Momma & Izumi, 2011).

α-P$_4$. The reduction of symmetry in δ-P$_4$ is accompanied by twinning. A further distinction can be found in the densities, with a value of 1.96 g cm^{-3} for δ-P$_4$ at 100 K but only 1.83 g cm^{-3} at 100 K in α-P$_4$, based on the data we collected from the soft plastic crystals (see above), assuming 58 tetrahedra in a unit cell.

With the new δ-P$_4$ polymorph stable at ambient conditions, its energetic relationships to the other known polymorphs remained to be determined. Accordingly, the relative stabilities of the different polymorphs of phosphorus have been computed by density-functional theory (DFT) methods, employing the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE) (Perdew *et al.*, 1996, 1997). Since dispersion corrections are known to be important for elemental phosphorus (Aykol *et al.*, 2017), not only uncorrected PBE calculations but also D3 and D3/BJ dispersion corrections, as developed by Grimme and coworkers, have been performed (Grimme, 2006; Grimme *et al.*, 2010, 2011).

Taking black phosphorus as the reference, the relative binding energies (Table S2) show that the correct order of stability can only be achieved by including dispersion corrections, in agreement with previous work (Aykol *et al.*, 2017). Further, the energetic ordering of γ-P$_4$ and δ-P$_4$ changes from PBE to PBE-D3, but the absolute value of the energy difference is very small. Becke–Johnson (BJ) damping increases the energy difference significantly. Consistent with previous theoretical studies (Aykol *et al.*, 2017; Bachhuber *et al.*, 2014) on a number of the polymorphs, the D3 and D3/BJ values show that the individual P$_4$ moieties are held together by van der Waals forces, resulting in metastable γ-P$_4$ and δ-P$_4$ polymorphs.

4. Conclusions

We have determined the crystal structure of a new polymorph of white phosphorus which resembles the structure of α-Mn. This similarity has already been described for α-P$_4$ (von Schnering, 1981). However, many other aspects of α-P$_4$ do not apply to our crystals of the new δ-P$_4$ polymorph. While the former crystallizes from CS$_2$, the latter crystallizes from dry, degassed hexane. The structure refinement of cubic α-P$_4$ is precluded by rotational disorder, but the orthorhombic δ-P$_4$ polymorph was refined without disorder despite serious twinning. Additionally, the two forms differ in their densities. From DFT calculations it can be concluded that γ-P$_4$ and δ-P$_4$ are metastable and that the twinning of δ-P$_4$ is energetically favourable. The description of the new polymorph significantly extends our knowledge of phosphorus.

5. Related literature

The following references are cited in the supporting information: Belsky *et al.* (2002); Bruker (2021*a*,*b*); Herbst-Irmer (2016); Kottke & Stalke (1993); Kresse & Furthmüller (1996); Kresse & Joubert (1999); Schulz *et al.* (2009); Sheldrick (2015*a*,*c*).

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