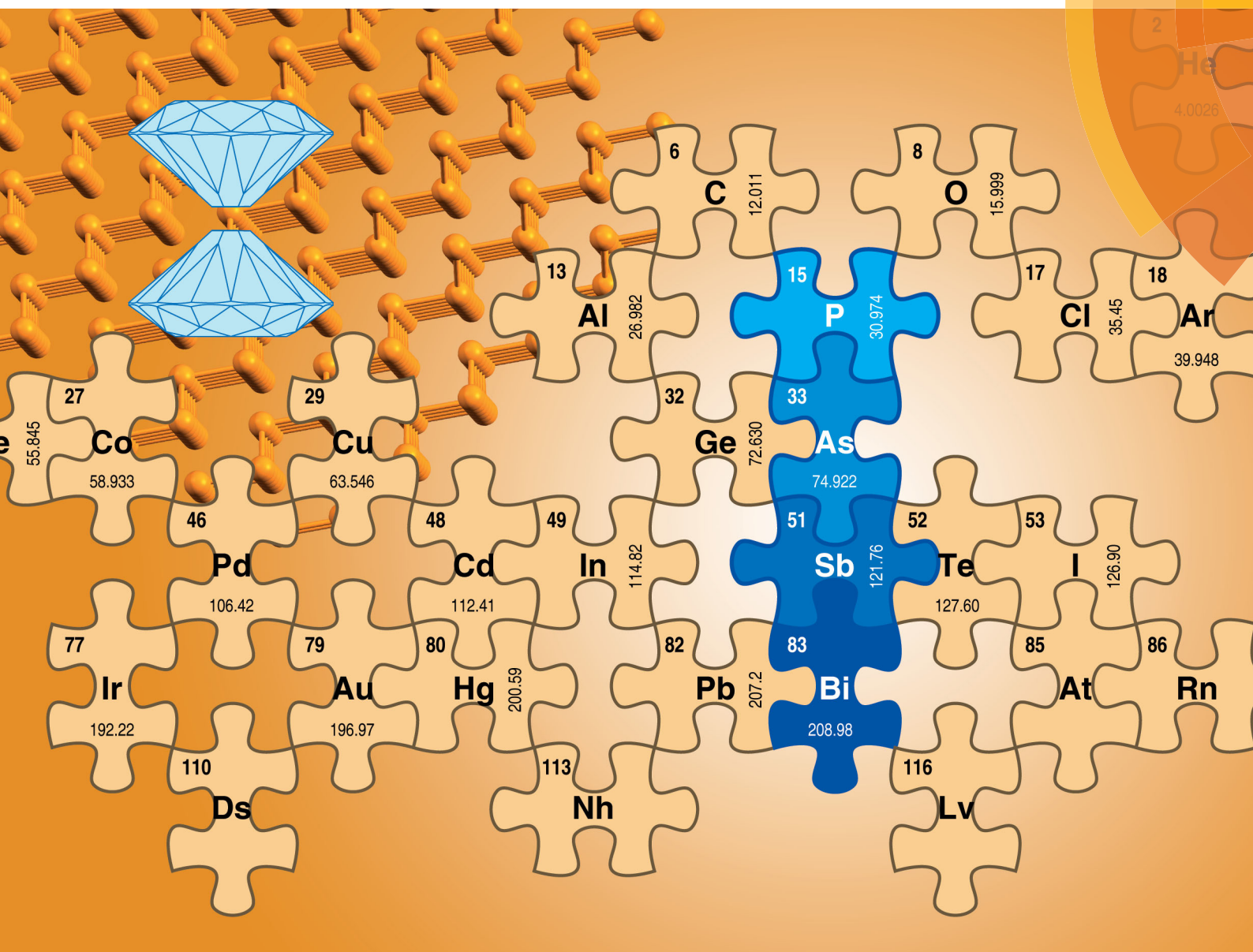


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The p-sc structure in phosphorus: bringing order to the high pressure phases of group 15 elements†

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Black phosphorus was studied by state-of-the-art synchrotron X-ray diffraction in a Diamond Anvil Cell during room temperature compression in the presence of He, H₂, N₂ and Daphne Oil 7474. The data demonstrate that the existence of the pseudo simple-cubic (p-sc) structure above 10.5 GPa is an intrinsic feature of P independent from the pressure transmitting medium. In the case of He, the pressure evolution of the lattice parameters and unit cell volume of P across the A17, A7 and p-sc structures was obtained and the corresponding EOS derived, providing a deeper insight on the recently reported p-sc structure. The results presented in this letter highlight the key role of the s–p orbital mixing in the formation and stabilization of the p-sc structure up to ~30 GPa, solving apparent contradictions emerging from previous literature and finally bringing order to the sequence of the high pressure A7 layered structure in group 15 elements.

The sequence of the high pressure structures of phosphorus at room *T* represents a striking anomaly in comparison to the other group 15 elements having higher atomic number. P is indeed the only element of the group exhibiting the A17 orthorhombic layered structure (*Cmce*, *Z* = 8),^{1,2} commonly known as black phosphorus (bP), which is actually the thermodynamically stable allotrope of the element at ambient conditions and currently represents the starting material for the synthesis of phosphorene^{3,4} (ESI†). In contrast, As, Sb and Bi crystallize in rhombohedral A7 (*R3m*, *Z* = 2), another layered structure adopted by P only above ~5 GPa, which can be described in this case by the stacking of blue phosphorene

layers.⁵ Furthermore, whereas the high pressure limit of the A7 structure decreases in the group with increasing atomic number, according to current literature its pressure value in P (11 GPa) is located below that of As (25 GPa).^{6,7} In both A17 and A7 layered structures each P atom hosts an electron lone pair and is three-coordinated to atoms belonging to the same layer, with three longer interatomic distances with respect to atoms in the adjacent layers.

Above 10.5 GPa the layered A7 structure is reported to transform to a metallic non-layered simple-cubic structure (*sc*, *Pm3m*, *Z* = 1) stable up to 103 GPa, in which P is hexa-coordinated with six equivalent interatomic distances⁸ (ESI†).

Recently, a synchrotron X-ray diffraction (XRD) study has shed new light on the phase diagram of P, demonstrating the presence of a two-step mechanism for the A7 to *sc* transition and unveiling the existence of an intermediate pseudo simple-cubic (p-sc) structure in the pressure range extending from 10.5 GPa up to at least ~30 GPa⁹ (ESI†). Indeed, adopting a rhombohedral cell description (*R3m*) for both A7 and *sc* structures, whereas above 10.5 GPa the angle α rapidly approaches the ~60° limit value characteristic of the *sc* structure, at ~30 GPa the atomic position *u* is still far from the 0.250 value expected in the *sc* structure, thus causing a metric pseudo-symmetry⁹ (Fig. 3, upper panel and Fig. 4 in ref. 9). The existence of the p-sc structure, originating from a pressure dependent competition between the s–p mixing and the electrostatic contribution, has two remarkable implications. First, from a chemical point of view, the presence of three shorter and three longer interlayer distances, in contrast with the six equivalent ones expected in the *sc* structure, structurally relates p-sc to A7, thus significantly raising the pressure limit where the layered phases of P exist. Second, the observation of the p-sc structure has provided new experimental evidence to explain the long-debated anomalous pressure evolution of the superconducting critical temperature *T_c* in P below 30 GPa.^{10–12} Experimental data indicate a maximum of *T_c* at ~30 GPa. Nevertheless, whereas calculations assuming a *sc* structure satisfactorily reproduce the pressure evolution of *T_c* above this limit, they catastrophically fail at lower pressure. The existence of the p-sc structure in this pressure range, responsible for a

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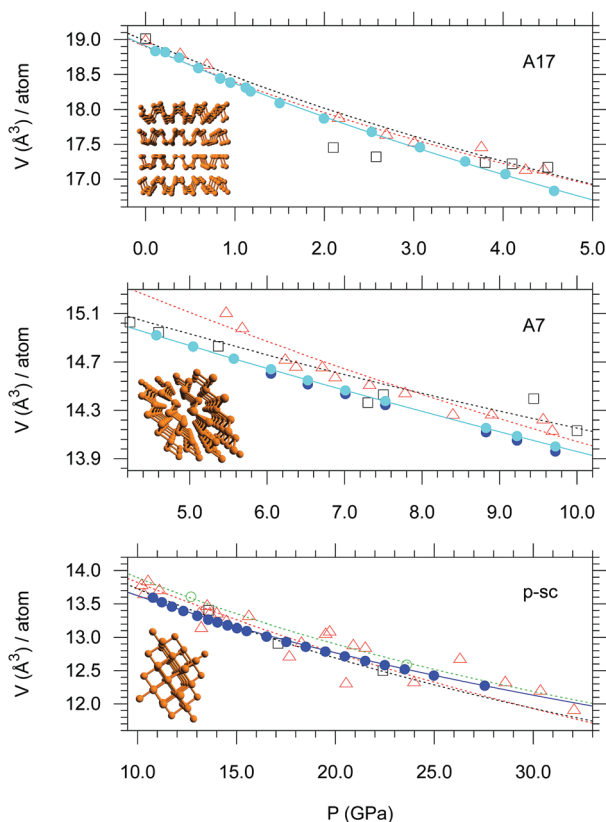


Fig. 2 EOS of bP in the A17, A7 and p-sc pressure ranges. The solid circles (cyan and blue) represent the data acquired in this study during the compression of bP using He as PTM. The blue points were obtained by Rietveld refinement of the XRD data. Empty symbols refer to the data reported by Kikegawa *et al.*¹⁷ (red triangles), Clark *et al.*¹⁸ (black squares) and Akahama *et al.*⁸ (green circles). The corresponding EOS type and fit parameters are indicated in Table S1 (ESI†). A drawing of each structure, obtained by a cif file in the corresponding pressure range, is also shown.

transitions^{20,21} (Fig. 3, lower panel). Even if both A7 and p-sc structures are described by a rhombohedral cell and no high or low symmetry phase can be strictly identified, the p-sc one is certainly more similar to the high symmetry sc structure. This observation provides conclusive evidence of the first order character of the A7 to p-sc structural transformation (ESI in ref. 9).

The high pressure structures in group 15 elements have been thoroughly studied due to the appearance of characteristic occurrences, like the rarely observed sc structure in P and As and the presence of incommensurate host-guest structures in the heavier elements.⁷ However, among the group peculiarities, two of them, both involving P, evidently stand out. The first one is related to the existence of the A17 structure. Indeed, with the exception of N, all the heavier pnictogens (P, As, Sb and Bi) exhibit crystalline layered structures at ambient conditions. Nevertheless, whereas the thermodynamically stable structure of P at ambient conditions is orthorhombic A17, As, Sb and Bi crystallize at ambient conditions adopting the rhombohedral A7 structure,^{6,7} which appears in P only above 4.8 GPa (Fig. 4). Structurally, A17 in P represents an isolated exception in group 15 elements. The second one concerns the high pressure limit

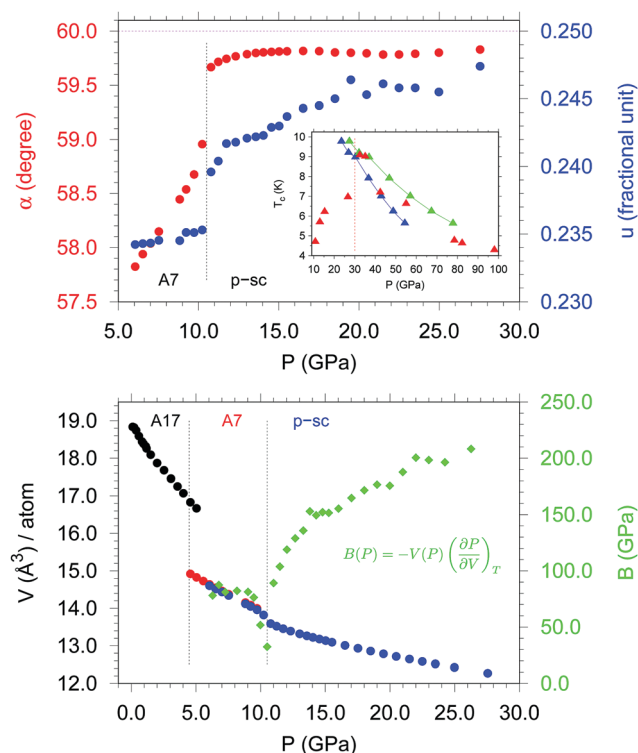


Fig. 3 Upper panel: Room *T* pressure evolution of the angle α (red) and atomic position u (blue) of the rhombohedral cell ($R\bar{3}m$) in the A7 and p-sc structures of P, with the magenta dotted line indicating their limit values in the sc structure (respectively 60 and 0.250) and the black dotted line marking the formation of p-sc at 10.5 GPa. The inset, adapted from ref. 22, shows the anomalous pressure evolution of experimental T_c (red triangles),¹² exhibiting a maximum at ~ 30 GPa, in contrast to calculations assuming a sc structure (blue and green triangles),²² with the dotted line marking the room *T* pressure limit up to which p-sc has been instead demonstrated to exist.⁹ Lower panel: Room *T* pressure evolution of the atomic volume (left y axis) of P across the A17 (black), A7 (red and blue) and p-sc (blue) structures and of the bulk modulus (right y axis) across the A7 and p-sc structures (green). The blue solid circles refer to the data obtained by Rietveld refinement in the A7 and p-sc structures. The minimum in the pressure evolution of the bulk modulus at 10.5 GPa, corresponding to the onset of the A7 to p-sc transformation,⁹ highlights the characteristic anomalous behavior reported for first order structural phase transitions.^{20,21}

for the A7 structure ($R\bar{3}m$, $Z = 2$), which in P, As, Sb and Bi is the last high pressure structure showing evidence of layers. Whereas in As (25 GPa), Sb (8.2 GPa) and Bi (2.55 GPa) this pressure limit decreases with increasing atomic number Z , according to literature the A7 structure in P, appearing at ~ 5 GPa, only extends up to 10.5 GPa, apparently contrasting the trend of the other elements (see dotted line in Fig. 4).

The observation of the p-sc structure and the identification of the effects responsible for its formation provide the key to interpret and reconsider these two anomalies. As emphasized by adopting the same rhombohedral cell description ($R\bar{3}m$), the p-sc structure is indeed structurally related to A7, featuring three shorter and three longer interatomic distances, thus extending the high pressure limit for the layered structures of P up to at least 30 GPa. This experimental observation places this limit for an A7-like structure in P above the corresponding



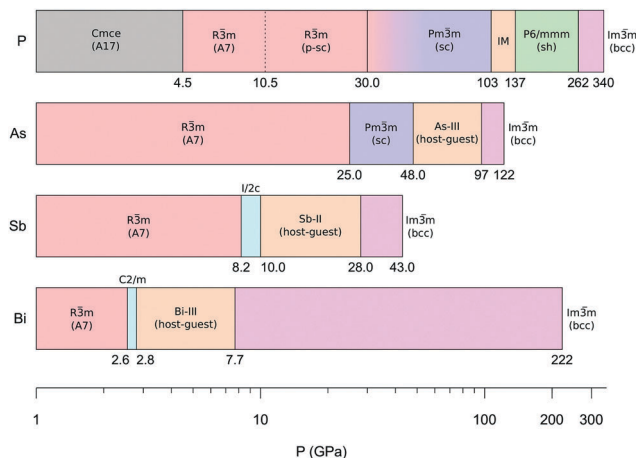


Fig. 4 High pressure phases of group 15 elements. Data were taken from literature ref. 7 and references therein, except for the A17, A7 and p-sc structures of P.⁹ The dotted line in P indicates the A7 to sc transition pressure previously reported in literature. The observation of the p-sc structure up to at least 30 GPa extends the existence of a rhombohedral unit cell ($R\bar{3}m$) above the pressure limit where the same cell is reported in As. For all the elements the high pressure limit of the bcc structures ($Im\bar{3}m$) represents the highest experimental pressure at which this structure has been observed.

A7 limit for As, bringing order to the sequence of the A7 high pressure limits in group 15 elements, which now decreases down in the group with increasing atomic number (Fig. 4). From a chemical point of view, this occurrence consistently relates to the interpretation provided for the existence of the p-sc structure in P as a consequence of the stronger s-p orbital mixing compared to higher Z elements. The extent of the s-p mixing in P is indeed such as to stabilize the A17 structure at ambient conditions, as explained by Seo and Hoffmann,²³ and decreases in the group with increasing atomic number, mirroring the A7 high pressure limit.

In summary, high quality XRD data about the A17, A7 and p-sc structures of bP, acquired up to ~ 30 GPa using different PTMs, are presented in this study, demonstrating that the p-sc structure is an intrinsic feature of the element and that a first order transition characterizes its formation. The results correlate the p-sc structure in P to the A7 structure in As, Sb and Bi, bringing order to the sequence of the high pressure limit for the A7 structure in group 15 elements as a function of the atomic number, thus solving a long-debated inconsistency within the group, which has fundamental relevance in the structural chemistry of the elements^{6,7} and potential applicative implications for the synthesis, functionalization and stabilization of phosphorene based materials and heterostructures. Once more, like in the case of C for group 14²⁴ and O for group 16,^{25,26} pressure has been shown here to be an extremely powerful tool for tuning the electronic properties of matter, thus enhancing the similarities between the structural and chemical properties of the lighter and heavier elements belonging to the same group and reconciling apparent discrepancies in their ambient pressure properties.

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Conflicts of interest

There are no conflicts to declare.

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