High pressure structure and chemistry of layered phases of Phosphorus

D.Scelta[1;2]*, A. Baldassarre[3], K. F. Dziubek[1;2], M. Serrano-Ruiz[2], A. B. Cairns[4], G. Garbarino[4], V. Svytlik[4], M. Peruzzini[2], R. Bini[1;2;3] and M. Ceppatelli[1;2]

[1] *LENS, European Laboratory for Non-Linear Spectroscopy, Via N. Carrara 1, I-50019 Sesto Fiorentino (FI), Italy*
[2] *ICCOM-CNR, Institute of Chemistry of OrganoMetallic Compounds, National Research Council of Italy, Via Madonna del Piano 10, I-50019 Sesto Fiorentino (FI), Italy*
[3] *Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze, Via della Lastruccia 3, I-50019, Sesto Fiorentino (FI), Italy*
[4] *ESRF, European Synchrotron Radiation Facility, B.P.220, F-38043 Grenoble Cedex, France*

Keywords: high pressure, chemistry, x-ray diffraction, spectroscopy.

*e-mail: scelta@lens.unifi.it

Phosphorus (P) is a key element for chemistry, physics, biology and Earth and planetary sciences [1], that exists in several allotropes with very different properties. In the recent years, a great interest has grown in the scientific community towards the synthesis, stabilization and functionalization of Phosphorene, a promising 2D platform material obtained from the exfoliation of layered crystalline black Phosphorus (bP) [2,3]. In this perspective, the layered phases of P are of special interest, and particularly orthorhombic A17, which is the stable allotrope of the element at ambient conditions, and rhombohedral A7, obtained by room temperature compression of A17 above ≈5 GPa and whose single layer is referred to as blue phosphorene. On further compression above ≈11 GPa, the A7 allotrope was reported to transform into a simple-cubic (sc), non-layered structure. A recent high pressure study [4] has allowed to gain fundamental insight about the mechanism ruling the formation of chemical bonds between P layers, unveiling the existence of an intermediate p-sc structure between the layered rhombohedral A7 and the non-layered simple-cubic phases of P, significantly raising the pressure limit where layered phases of P can be observed up to at least 30 GPa, with great implications not only for the phase diagram itself but also for the superconducting behaviour of P. Furthermore, we have shown [5] that p-sc structure is an intrinsic feature of P, that does not depend on the pressure transmitting media, and at the same time we derived the Equation of State for A17, A7 and p-sc phases. In addition, the A7 to p-sc transition was demonstrated to follow a first order mechanism. Highlighting the structural relations between A7 and p-sc, we were finally able to solve the apparent contradictions emerging from previous literature data, bringing order to the sequence of HP A7 layered structures in group 15 elements [5]. Besides the structural features, also the study of reactive behaviour of P is of great interest for what is concerned with its stability. In this framework, we studied the high pressure and high temperature chemistry of Phosphorus in the presence of simple molecular systems (NH_3, N_2). Besides the N functionalization of Phosphorene layers, this kind of studies are relevant to the substantially unexplored chemistry of the low Z pnictogens and to the synthesis of new PN compounds [6].

Acknowledgments: Thanks are expressed to EC through the European Research Council (ERC) for funding the project PHOSFUN "Phosphorene functionalization: a new platform for advanced multifunctional materials" (Grant Agreement No. 670173) through an ERC Advanced Grant.

[1] D. E. C. Corbridge, Phosphorus Chemistry, Biochemistry and Technology (CRC Press, 2013).
[2] M. Batmunkh et al., Adv. Mater. 28, 8586 (2016).
[3] M. Peruzzini et al., Eur. J. Inorg. Chem., 2019 (11-12), 1476 (2019).
[4] D. Scelta et al., Angew. Chem. Int. Ed. 56, 14135 (2017).
[5] D. Scelta et al., Chem. Commun., 54, 10554 (2019)..
[6] D. Scelta et al., submitted (2018).