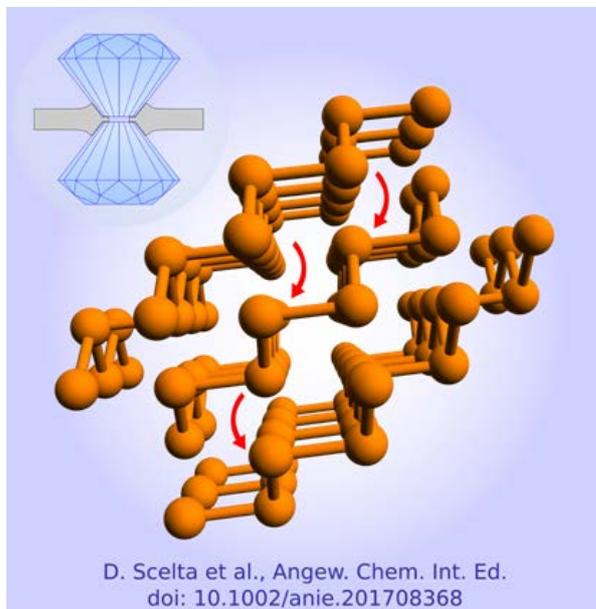


Interlayer Bond Formation in Black Phosphorus at High Pressure



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Abstract:

In this study we report the first experimental observation of the two-step mechanism leading to the formation of interlayer bonds in Phosphorus at high pressure. The results indicate the existence of an intermediate pseudo simple-cubic (p-sc) structure between the layered A7 and the non-layered sc phases. The presence of two different values of interatomic distances relates p-sc to A7, significantly raising the pressure limit for the layered phases of Phosphorus, with remarkable implications for the synthesis, stabilization and functionalization of Phosphorene based systems and for the superconductivity of Phosphorus in this pressure range.

Phosphorus is well known to chemists for exhibiting a variety of solid structure at ambient pressure. These structures feature very different chemical and physical properties and are typically referred to by their color (i.e. white, red, violet and black). Among them black Phosphorus, first synthesized at high pressure by Bridgman back in 1914, is currently attracting strong and growing attention from the scientific community. The recent synthesis of Phosphorene, a 2D corrugated monoatomic layer of P atoms with extraordinary properties, has indeed dramatically raised the interest of chemists, physicists and materials scientists about the layered phases of this element [1]. In fact the crystalline structure of black Phosphorus (A7) is actually made by the stacking of Phosphorene lay-

ers, in a similar way as Graphene is related to Graphite and black Phosphorus is the starting material for obtaining Phosphorene. Nevertheless the synthesis, stabilization and functionalization of single layer Phosphorene still represent very challenging tasks. Within this perspective, the knowledge of the effects that play a key role in stabilizing the layered vs non-layered structures of Phosphorus and the understanding of the mechanism of interlayer bond formation become extremely important for designing and synthesizing Phosphorene based materials and heterostructures. Pressure is the ideal tool for studying this kind of processes because it allows a fine control to increase the density of matter, reducing the interatomic distances up to induce chemical reactivity.

Under room temperature compression the layered structure of black Phosphorus (A7) is stable up to ~ 5 GPa, where a redistribution of the electronic density with bond breaking and reconstruction converts it to another layered structure (A7) stable up to ~ 11 GPa. Here, according to literature, a transition to the non-layered sc phase, with 6 equivalent interatomic distances, takes place. This transition is particularly important because the associated bond breaking and reconstruction mechanism sets the stability limit for the layered phases of Phosphorus.

Exploiting the advantages of state-of-the-art synchrotron XRD at ESRF-ID27, using a membrane Diamond Anvil Cell (DAC) and He as hydrostatic pressure transmitting medium, we performed a room temperature compression of black Phosphorus up to 27.6 GPa, across the A17, A7 and sc phases. The observation of two previously unreported extra peaks in the diffraction pattern of the sc structure, persisting up to the highest investigated pressure, lead us to a revision of the Phosphorus phase diagram up to 30 GPa.

This experimental work, in collaboration between ICCOM-CNR and LENS, gives for the first time a deep insight into the mechanism of interlayer bond formation in black Phosphorus at high pressure. In excellent agreement with theoretical predictions [2], our data, acquired at ESRF, demonstrate the existence of a two-step mechanism for the A7 to sc phase transition. In the first step the hexagonal lattice of the A7 phase, rapidly converts to a distorted simple-cubic lattice at 10.5 GPa. The angle α almost immediately reaches the limit value of 60.0° , but the atoms do not occupy the positions expected in the sc structure. In the second step, not yet completed at 27.6 GPa, α remains constant and the atoms slowly

move in pressure towards the positions expected in the sc structure ($u \leq 0.250$). Correspondingly, a first ($d1$) and a second ($d2$) nearest neighbor distances, both referred to three atoms, are observed, instead of the single value, expected in the sc structure, corresponding to an octahedral coordination with 6 equivalent atoms. Notably, $d1$ and $d2$ do not converge at the highest pressure, consistently with the pressure evolution of u .

These observations imply that, in the pressure range from 10.5 up to at least 27.6 GPa, a pseudo simple-cubic (p-sc) structure exists rather than the sc one (Figure 2). Theoretical studies indicate that at low pressure a strong s - p orbital mixing is responsible for the presence of electron lone pairs at Phosphorus atoms and for the formation of layers in the A17 and A7 structures, whereas at high pressure, under higher density conditions, the electrostatic contribution becomes dominant, leading to the octahedral coordination with six nearest neighbor distances typical of the sc structure. However, for intermediate pressure, the dependent competition between these two effects generates the p-sc structure, with remarkable implications.

From a chemical point of view, the presence of three shorter and three longer interatomic distances structurally relates p-sc to A7, significantly raising the pressure limit for the layered phases of Phosphorus. Furthermore, the knowledge of the mechanism of the A7 to sc phase transition and the comprehension of the effects that determine it open new perspectives for the synthesis, stabilization and functionalization of Phosphorene based systems.

On the other side, as superconductivity is concerned, the identification of the p-sc structure in the 10-30 GPa range provides new experimental evidence to explain the long-debated anomaly in the pressure evolution of the critical temperature T_c in the sc phase.

Acknowledgements

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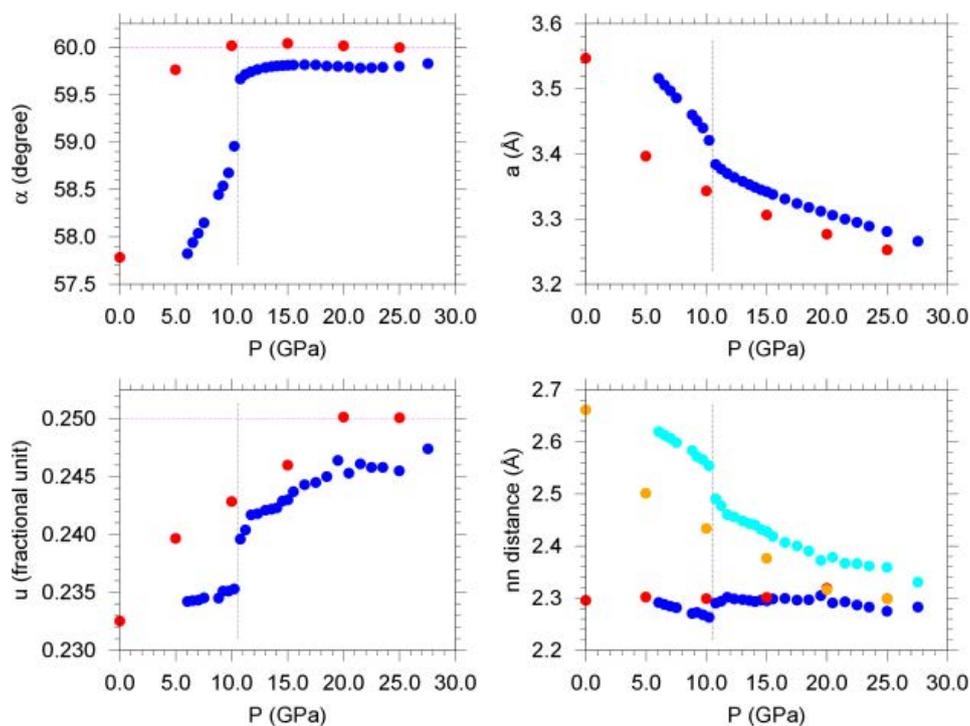
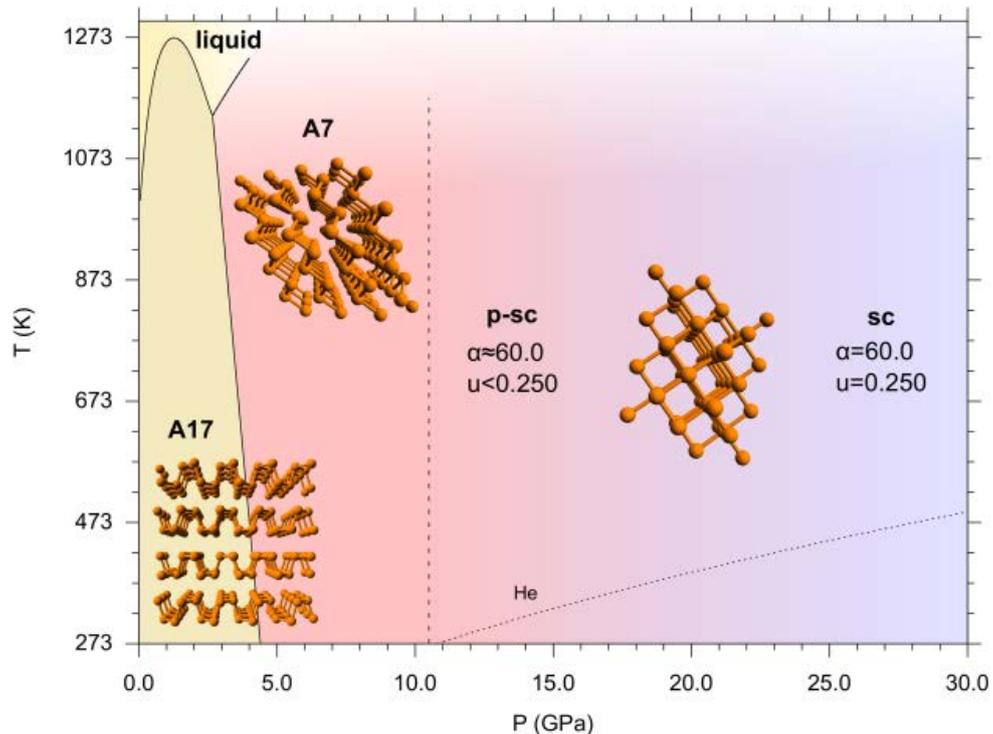


Figure 1. Pressure evolution of the angle α (upper left panel), the fractional atomic position u (lower left panel), the lattice parameter a (upper right panel), and the nearest neighbor distances nn (lower right panel) across the A7 to sc phase transition of Phosphorus. The blue points indicate the experimental data of this study, whereas the red points are the calculated values extracted from ref. [2]. In the case of nn the blue and cyan points respectively indicate the experimental first ($d1$) and second ($d2$) nearest neighbor distances, whereas the red and orange points respectively indicate the calculated first and second nearest neighbor distances.

The dashed vertical line at 10.5 GPa indicates the A7 to sc phase transition reported in literature. The two dashed horizontal magenta lines at 60.0 degree (left upper panel) and at 0.250 fractional unit (left lower panel) indicate the limiting values of these quantities once the transition from the A7 to the sc phase is completed (D. Scelta, et al. *Angew. Chem. Int. Ed.* 2017, DOI: 10.1002/anie.201708368, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

Figure 2. Phase diagram of Phosphorus between 0.0 and 30.0 GPa, showing the pressure and temperature ranges where A17 and A7 are reported to be stable. The dashed line at 10.5 GPa marks the A7 to sc phase transition according to current literature. Our room T data indicate that the sc phase is not achieved up to 27.6 GPa and that an intermediate pseudo simple-cubic (p-sc) structure exists between the A7 and the sc structures. The melting line of He is also displayed (dotted line). Structures generated by the Rietveld refinement of our data in the corresponding phases are also shown, highlighting the transition between the A17 and A7 layered structures and the transformation of layered A7 to non-layered sc (D. Scelta, et al. *Angew. Chem. Int. Ed.* 2017, DOI: 10.1002/anie.201708368, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).



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