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Supporting Information

Interlayer Bond Formation in Black Phosphorus at High Pressure

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Supporting Information

SI-1. Phosphorene

In contrast to Graphene, where doping is required for introducing a bandgap in view of potential applications in electronic devices, Phosphorene inherently features a natural bandgap, which can be further and suitably adjusted by tuning the number of stacked layers (from 0.3 eV to 2.0 eV, respectively in bulk bP and Phosphorene), thus immediately attracting a growing interest from the chemists, physicists and materials scientists communities, envisaging a large variety of applications including field-effect transistors, gas sensing and catalysis.[1–5] Even if the synthesis, stabilization and functionalization of single layer Phosphorene still represent challenging tasks,[6] new single layer allotropes with intriguing properties, including Hittorphene[7] and blue Phosphorene,[8] respectively related to Hittorf's and high pressure A7 Phosphorus, have been predicted to be stable.

SI-2. Evolution of the XRD peaks during the compression

Pressure was slowly increased in steps of a few tenths of GPa, waiting for pressure stabilization before the next pressure change. XRD patterns were acquired at every pressure value, to obtain informations on the pressure evolution of the unit cell volume and on the lattice parameters across the A17 to A7 and the A7 to sc phase transitions

The peak positions of Phosphorus in the three phases, shown in Figure 2, are in agreement with literature data.[9–14] The relative intensity variation of the diffraction peaks observed in some spectra, compared to literature data, is related to the preferred orientations of the bP grains in the polycrystalline starting material and to the small X-ray beam diameter with respect to the particle size, affecting the powder average.

A17

During the compression the separation between the $(040)_{A17}$ and $(111)_{A17}$ reflections become smaller with increasing pressure and the two peaks convolute into a single one at about 2 GPa. Between 0.2 and 1.5 GPa the $(042)_{A17}$ reflection moves from lower to higher 2θ values with respect to the $(200)_{A17}$ one, which, however, is the only reflection not appreciably shifting upon increasing pressure.

Kikegawa and coauthors[15] reported this transition to be accompanied by some hysteresis. Indeed they could observe the peaks of the A17 structure up to ∼2 GPa after the appearance of the A7 ones. Our data are in agreement with those of Kikegawa and coauthors,[15] as we could detect traces of the A17 phase up to ∼7 GPa.

A17 to A7

The formation of the A7 phase between 4.6 and 5.0 GPa is indicated by the appearance of two new peaks corresponding to the 003_{A7-h} and 101_{A7-h} reflections, which become particularly evident at 6.5 GPa (2θ values respectively of 7.3667 ± 0.0005 and 7.686 ± 0.002 degree). The appearance of the A7 peaks is associated to the disappearance of the A17 reflections, which is immediately appreciable in the case of the 020_{A17} and 021_{A17} peaks.

A7 to sc

The formation of a new phase is clearly visible in the case of isolated peaks, as demonstrated by the sudden appearance of the 200_{sc} reflection and by the corresponding disappearance of isolated peaks of the A7 phase (101_{A7-h}, 015_{A7-h}, $11\bar{1}_{A7-h}$ and 024_{A7-h}), but can be appreciated also in 2θ regions, where a more subtle transformation of the overlapping peaks of the A7 phase into those of the sc one occurs ($012_{A7-h} \rightarrow 100_{sc}$, $110_{A7-h} \rightarrow 110_{sc}$ and $202_{A7-h} \rightarrow 111_{sc}$).

Further considerations

Two recent papers, appeared during the writing of this manuscript,[16,17] report anomalies in the structural evolutions from the A17 up to the simple-cubic phases, which however are likely related to the non hydrostaticity of the employed pressure transmitting media and to the use of exfoliated few layer bP nanosheets.[16] None of the two papers mentions the presence of extra reflections in the diffraction pattern above 10.5 GPa.

Table SI-1: Parameters of the p-sc structure ($R\bar{3}m$) obtained by the Rietveld refinement of the XRD patterns acquired during the compression.

T (K)	P (GPa)	a (Å)	α (degree)	u	U$_{iso}$	d_1 (Å)	d_2 (Å)	wR factor
298	6.05	3.516(5)	57.823(7)	0.2342(2)	0.054(1)	2.292(1)	2.6198(2)	0.01152
298	6.525	3.506(5)	57.939(7)	0.2343(2)	0.053(1)	2.288(1)	2.6130(2)	0.01152
298	7.01	3.497 (5)	58.037(7)	0.2343(2)	0.052(1)	2.285(1)	2.6071(2)	0.01082
298	7.525	3.486(5)	58.148(7)	0.2345(2)	0.056(1)	2.282(1)	2.5986(2)	0.01063
298	8.825	3.460(5)	58.446(7)	0.2345(2)	0.059(1)	2.271(1)	2.5835(2)	0.00985
298	9.225	3.451(5)	58.538(7)	0.2351(3)	0.060(1)	2.273(1)	2.5719(2)	0.01035
298	9.72	3.440(5)	58.676(7)	0.2351(3)	0.059(1)	2.268(1)	2.5658(2)	0.01049
298	10.23	3.42(1)	58.96(2)	0.2353(5)	0.056(2)	2.263(2)	2.5540(3)	0.01772
298	10.775	3.384(6)	59.667(9)	0.2396(4)	0.065(1)	2.290(2)	2.4909(2)	0.01239
298	11.23	3.377(5)	59.716(7)	0.2404(4)	0.066(1)	2.294(2)	2.4777(1)	0.01014
298	11.74	3.370(6)	59.744(9)	0.2417(5)	0.083(1)	2.302(2)	2.4605(2)	0.01231
298	12.315	3.364(6)	59.767(9)	0.2418(5)	0.085(1)	2.297(2)	2.4560(2)	0.01219
298	13.02	3.358(6)	59.787(9)	0.2421(5)	0.089(1)	2.297(2)	2.4483(2)	0.01291
298	13.57	3.353(7)	59.80(1)	0.2422(5)	0.093(2)	2.296(2)	2.4433(2)	0.01289
298	14.04	3.349(7)	59.80(1)	0.2423(5)	0.093(2)	2.293(2)	2.4406(2)	0.01331
298	14.545	3.345(7)	59.81(1)	0.2429(5)	0.098(2)	2.296(2)	2.4319(2)	0.01352
298	15.025	3.342(7)	59.81(1)	0.2430(5)	0.099(2)	2.295(2)	2.4279(2)	0.01356
298	15.515	3.338(7)	59.81(1)	0.2437(6)	0.010(2)	2.299(3)	2.4186(2)	0.01400
298	16.52	3.331(7)	59.82(1)	0.2443(7)	0.096(2)	2.300(3)	2.4069(2)	0.01414
298	17.52	3.324(6)	59.815(9)	0.2445(7)	0.095(2)	2.296(3)	2.4005(2)	0.01395
298	18.5	3.318(6)	59.803(8)	0.2450(7)	0.089(1)	2.297(3)	2.3906(2)	0.01334
298	19.495	3.312(5)	59.800(7)	0.2464(9)	0.088(1)	2.305(4)	2.3728(2)	0.01284
298	20.475	3.306(5)	59.795(7)	0.2453(7)	0.086(1)	2.291(3)	2.3787(1)	0.01228
298	21.505	3.300(4)	59.783(6)	0.2461(8)	0.082(1)	2.293(4)	2.3673(1)	0.01200
298	22.495	3.295(5)	59.784(8)	0.2460(1)	0.079(1)	2.287(4)	2.3663(2)	0.01523
298	23.505	3.289(4)	59.791(6)	0.2458(8)	0.077(1)	2.283(3)	2.3619(1)	0.01197
298	24.98	3.281(4)	59.801(6)	0.2455(7)	0.073(1)	2.275(3)	2.3593(1)	0.01226
298	27.55	3.266(4)	59.830(5)	0.247(1)	0.072(9)	2.283(5)	2.3310(1)	0.01188

SI-3. Bragg indexing of the A7 and p-sc XRD patterns

Literature inconsistently refers to the A7 phase in terms of the structurally equivalent rhombohedral or hexagonal cell. For consistency with our treatment, in the following we will adopt the rhombohedral cell description. Nevertheless, we refer to the diffraction peaks using the Bragg indexes corresponding to the hexagonal cell for three reasons: first, the hexagonal cell allows a visually more intuitive identification of the P layers; second, literature mostly relies on this cell settings for peak indexing and comparison is thus easier; third, convenient structural information can be straightly extracted. However, to help the reader, r and h labels have been used to indicate the indexing respectively according to the rhombohedral (A7-r) or hexagonal (A7-h) cell, and a correspondence between the two peak indexing is reported in Table SI-2.

A list of the reflections observed for the p-sc structure, indexed according to the rhombohedral cell ($R\bar{3}m$), is reported in Table SI-3.

rhombohedral	hexagonal
111	003
100	101
110	012
211	104
$10\bar{1}$	110
221	015
210	113
222	006
$11\bar{1}$	021
200	202
220	024
322	107
311	205
321	116
$21\bar{1}$	102

Table SI-2: Correspondence between Bragg indexes of the reflections of the A7 structure in terms of rhombohedral and hexagonal cells, fulfilling the condition -H+K+L= 3n, where H= h-k, K= k-l, L= h+k+l, with hkl and HKL respectively representing the Bragg indexes of the Rhombohedral and Hexagonal cells (see Table A1.4.4.1 in ref.[18] for equivalent reflections).

p-sc	
hkl	d-spacing
111	2.76321
100	2.74742
110	2.38273
211	1.68847
$10\bar{1}$	1.68125
221	1.44078
210	1.43628
$11\bar{1}$	1.43405
222	1.38161
200	1.37371
220	1.19137
322	1.09699
311	1.09401
$20\bar{1}$	1.09106
321	1.06742
$21\bar{1}$	1.06377
332	0.97624
310	0.972052
$2\bar{1}\bar{1}$	0.970668
333	0.921071
331	0.91872
320	0.916969
$22\bar{1}$	0.915806
300	0.915806

Table SI-3: Bragg indexes (according to a rhombohedral $R\bar{3}m$ cell) and calculated d-spacing values of the p-sc structure at 11.2 GPa obtained by the Rietveld refinement of our data.

SI-4. The origin of the 003_{A7-h} and 113_{A7-h} "extra peaks"

The intensity of the two peaks, related to the 003_{A7-h} and 113_{A7-h} reflections, is weak, but definitely not negligible, furthermore their profile is slightly asymmetric.

The origin of these two peaks was carefully checked and verified. Initially, considering recent studies reporting the pressure induced insertion of small atoms and molecules within nanometric cavities of comparable size with respect to the interlayer spacing of the A17 and A7 structures of Phosphorus,[19–23] we possibly related the presence of these two extra reflections to the persistence of A7 domains, due to the pressure induced insertion of He atoms between the P layers, preventing the formation of interlayer bonds and hence the occurrence of the transition from the A7 to the sc structure. To exclude this possibility, we performed another experiment using a non-penetrating pressure transmitting medium (Daphne Oil 7474) of much larger size compared to He. Even if the non-hydrostaticity of the medium caused a deviatoric stress resulting in the broadening of the diffraction lines, the observation of the same two persisting reflections of the A7 phase within the pressure range of the sc one, allowed to definitely rule out the attribution of this effect to the pressure induced insertion of He atoms between the P layers.

Whereas all the previous studies used a variety of non hydrostatic pressure transmitting media (Fluorinert FC-75,[11] NaCl,[12] Boron + epoxy resin,[15] 16:4:1 ratio of methanol-ethanol-water[24]), the observation of the two extra peaks is, however, neither an issue related to the application of hydrostatic conditions, because we could observe them in two samples of bP with He, in one of bP with Daphne Oil 7474 and also in several samples of bP with other non-hydrostatic pressure transmitting media (thus also excluding a possible influence of the He solidification), nor to a specific batch of bP, because we successfully repeated the experiment starting from different crystalline bP samples and also using exfoliated bP, to exclude a possible role of defects.

Experimentally, literature data[15] have usually identified the occurrence of the A7 to sc transition by the merging of the 104_{A7-h} and 110_{A7-h} peaks into the 110_{sc} one,[15] apparently neglecting the behavior of the 003_{A7-h} and 113_{A7-h} reflections. Indeed, no mention about their persistence within the stability pressure range of the sc phase can be found in literature. Chan and coauthors[25] have followed the same approach to identify the occurrence of the phase transition and the merging of the 104_{A7-h} and 110_{A7-h} peaks into the 110_{sc} one can actually be clearly appreciated also in our patterns at 2θ ∼12.5 degree above 10.5 GPa (Figure 2 in the manuscript). Nevertheless, zooming in the XRD patterns simulated by Chan and coauthors[25] for the A7 phase at 10 and 15 GPa with $\alpha \approx 60$ degree and u respectively 0.243 and 0.246, weak intensities can be appreciated at 2θ ∼15 and ∼29 degree, which, taking into account the different wavelength, perfectly correspond to the two extra peaks observed in our patterns at the same pressure.

The description of the diffraction data in terms of a rhombohedral cell ($R\bar{3}m$) also accounts for the slight asymmetry of the two extra peaks, as the Rietveld refinement for this cell reveals the presence of overlapped reflections for both of them. In particular, the 003_{A7-h} and 113_{A7-h} reflections contain contributions respectively from the 111_{p-sc-r} and 100_{p-sc-r} reflections and from the 210_{p-sc-r}, 221_{p-sc-r} and $11\bar{1}_{p-sc-r}$ reflections, where the label *p-sc-r* refers the p-sc structure (see Table SI-2 for correspondences between the hexagonal and rhombohedral indexing and later in the manuscript for the p-sc structure).

A slight asymmetry, further confirming the distortion of the sc lattice, is also observed in the peak profile of the 111_{sc} reflection, where two contributions (222_{p-sc-r} and 200_{p-sc-r}) can be appreciated up to ∼16.5 GPa (Figure 3 in the manuscript).

SI-5. Calculation of the c/a ratio

The values of a and c were obtained from the $(003)_{A7-h}$ and $(113)_{A7-h}$ reflections by applying the following geometrical relation of the hexagonal cell for the corresponding Miller indexes at each pressure

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

The peak positions were determined by fitting the XRD spectra using Voigt line shapes, after baseline subtraction using Fityk software.[26]

SI-6. The order of the A7 to sc transition in literature

The mechanism of the A7 to sc transition has been investigated by several theoretical studies,[25,27–32] trying to account for some Phosphorus particularities compared to the other group 15 elements, like the existence of the A17 phase, the reduced pressure range for the stability of the A7 one and the formation of the rarely observed sc structure.

Interestingly, even if in some cases a higher pressure for the A7 to sc transition has been calculated[27,30] compared to the experimentally reported one,[12] with the exception of Chan and coauthors,[25] none of these studies predicted the existence of a pressure range where the p-sc structure could be stable.

Sasaki and coauthors[30] performed a detailed investigation about the mechanism of the A7 to sc phase transition, which substantially supports our data, as they calculated the cell distortion, corresponding to the α=60.0 degree condition, to be energetically negligible (0.02 mRy/atom) compared to the atom displacement (0.71 mRy/atom). Furthermore, within this assumption, they applied the Landau theory of phase transitions and concluded the A7 to sc transition to be of the II order, in contrast with the available experimental data,[15] reporting a sharp I order transition. Sasaki and coauthors identified the atomic displacement as the order parameter for the transition and developed an equation for the energy in terms of it (see Appendix in ref.[30]). Aware about the limitations of this approach,[33] we tried without success to fit our data, plotted as *u(V)*, where u is the atomic position and V the volume, with the following equation of u,

$$u = \left[\frac{\alpha}{c}(V - V_c) - \frac{b}{2c}\right]^{\frac{1}{4}} \tag{2}$$

obtained by imposing

$$\frac{\partial E}{\partial u} = au + \frac{1}{2}bu + cu^5 = 0 \tag{3}$$

A more recent theoretical study about the mechanisms of the phase transitions in group

15 elements[32] indicate the A7 to sc transition to follow a displacive mechanism. The authors point out that the A7 structure can be obtained via a small distortion of the sc one, followed by an atomic displacement, in agreement with previous studies and with our data. Applying symmetry considerations to the Laundau theory, they also noted that, whereas the second step is associated to a displacive order-parameter, the first one is associated to a secondary order parameter, which is not negligible compared to the first one, as instead assumed in ref.[30] The coupling of the secondary order-parameter with the displacive one imposes the I order character of the A7 to sc transition. This could explain the mismatch between our data and the mathematical fit using equation 2.

SI-7. T_c

More recent experimental data by Flores-Livas and coauthors about the pressure evolution of T_c have been loaded on arxiv,[34] but not published at the moment. In this report two pressure evolutions of T_c along a low and a high T compression paths are presented. The first one is in substantial agreement with Karuzawa and coauthors,[35] with a maximum position which is ∼5 GPa lower than the previous data. In the second one the maximum is less sharp and T_c reaches the highest values between 30-50 GPa, slowly decreasing for high pressure. In both cases the pressure behavior on the low pressure side of the maximum can be appreciated. However, it must be pointed out that red Phosphorus, instead of black Phosphorus, was loaded into the DAC by Flores-Livas and coauthors.

Theoretical calculations presented in the same report, trying to account for the pressure evolution of T_c, indicate the coexistence of multiple metastable phases (A17, A7 and sc) to play a role in Phosphorus superconductivity.

It should be emphasized that using different allotropes of Phosphorus as starting material, as also occurred in ref[24] where white P was loaded, can lead to contradictory results due to incomplete transformations. For this reason we have used bP, which is the thermodynamically stable allotrope of the element.[36]

Our XRD data, acquired during room T compression of bP, do not show any trace of the A17 peaks above 7-8 GPa. Above 10.5 GPa all the peaks corresponding to A7 phase disappear and the diffraction pattern resembles that of the sc phase, with the exception of the two extra reflections, leading to the identification of the p-sc structure, as reported and discussed in the main text.

Author contributions

D.S., M.C, A.B. and R.B. performed the experiments, analyzed the data and discussed the results. K.D. and M.P. analyzed the data and discussed the results. M.S.R. synthesized bP. A.C. assisted at ESRF-ID27. M.C. conceived the experiment and wrote the article.

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