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Editors' Suggestion

Hexagonal Layered Polymeric Nitrogen Phase Synthesized near 250 GPa

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The nitrogen triple bond dissociates in the 100 GPa pressure range and a rich variety of single-bonded polymeric nitrogen structures unique to this element have been predicted up to the terapascal pressure range. The nonmolecular cubic-gauche (cg-N) structure was first observed above 110 GPa, coupled to high temperature (>2000 K) to overcome the kinetic barrier. A mixture of cg-N with a layered phase was afterwards reported between 120 and 180 GPa. Here, by laser heating pure nitrogen from 180 GPa, a sole crystalline phase is characterized above 240 GPa while an amorphous transparent phase is obtained at pressures below. X-ray diffraction and Raman vibrational data reveal a tetragonal lattice ($P4_2bc$) that matches the predicted hexagonal layered polymeric nitrogen (HLP-N) structure. Density-functional theory calculations which include the thermal and dispersive interaction contributions are performed to discuss the stability of the HLP-N structure.

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Solid N_2 has been extensively studied as an archetype of the transformation of molecular solids under pressure. A rich phase diagram has been disclosed with fourteen structures reported so far [1]. Up to a few tens of gigapascals, the organization of the N_2 molecules is governed by compacity and a strong quadrupole-quadrupole van der Waals interaction [2]. Under pressure, the triple bond was predicted to rupture due to the rapid increase of the compressed molecule's kinetic energy and dense nitrogen was then expected to adopt the same crystal structure as isovalent black phosphorous or α arsenic [3,4]. But in 1992, Mailhot *et al.* proposed instead the stability of a unique structure above 50 GPa, the cubic-gauche polymeric nitrogen (cg-N), solely composed of single-bonded nitrogen atoms forming a three dimensional network [5]. Since then, many remarkable structures have been predicted up to a few terapascals for singly bonded polymeric nitrogen (poly-N) with chains, layers, cages, and ions [6–12]. A theoretical high pressure zero-temperature sequence appears acceptable today: $\text{cg-N}\xrightarrow[188\ \text{GPa}]{}\text{LP-N}\xrightarrow[263\ \text{GPa}]{}N_{10}\xrightarrow[2100\ \text{GPa}]{}Cmca$ metal $\xrightarrow[2500\ \text{GPa}]{}P4/nbm$ metallic salt, with the first three transformations corresponding to a nonintuitive sequence $3D \rightarrow 2D \rightarrow N_{10}$ *superatom* arrangement [6,11]. Below 160 GPa and above 300 GPa up to 2100 GPa, respectively, the cg-N and N_{10} structures are calculated to have a much lower enthalpy in their stability domain than the other structures found in the search. On the other hand, the layered $Pba2$ phase (LP-N) predicted stable in between 188–263 GPa is almost degenerate in energy (differing by less than 10 meV/atom) with a few single-bonded structures, including the $P4_2bc$, $P2_12_12_1$, and $Cmca$ [6].

The cg-N structure was observed in 2004 by Eremets *et al.* from 110 to 140 GPa above 2000 K [13]. Recently, Tomasino *et al.* reported a novel form of singly bonded nitrogen, called LP-N, synthesized by the direct laser heating of nitrogen between 126 and 175 GPa. However, the assignment of the $Pba2$ structure to LP-N has not yet been independently confirmed. This new phase was always obtained with a significant amount of cg-N along with the metastable $C2/c$ phase in smaller amounts [14]. Later, it was proposed that a mixture of cg-N, $Pba2$, and $Pccn$ single-bonded allotropes matches better the observed diffraction pattern, although not favored from the calculated enthalpy [10].

In this Letter, we investigate the structural transformation of solid nitrogen in the pressure range 180–250 GPa under direct laser heating. By going to higher pressure than previously reported, we aimed to go out of the stability field of cg-N and so obtain the next singly bonded nitrogen phase in a pure form. Indeed, a single crystalline phase was produced at 244 GPa. The structure corresponds to a tetragonal $P4_2bc$ arrangement formed of interconnected chains of nitrogen hexagons. The phase called hexagonal layered polymeric nitrogen (HLP-N) is characterized by both Raman spectroscopy and x-ray diffraction measurements and is found metastable at least down to 66 GPa. Further insights are provided on the properties of this new phase by density-functional calculations (DFT), which also present clues questioning the structural assignment of the LP-N phase.

Two pure molecular nitrogen samples were loaded at 1400 bars in diamond anvil cells equipped with diamond culets of 40 or 50 μm, reaching pressures of 230 and

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244 GPa, respectively. Prior to heating, both samples were compressed above 180 GPa where nitrogen is completely opaque and no x-ray diffraction peak nor Raman signature can be detected [15–18]. The sample could then be heated by the direct absorption of the laser radiation. Laser heating the sample to 1200 K at 209 GPa was noticed to make the nitrogen sample partially transparent. Yet, no x-ray diffraction peaks or vibrational modes appeared. Extending laser-heating temperatures and pressures to 2800 K and 231 GPa further increased the sample's transparency but still no diffraction peaks could be distinguished. The nitrogen sample was thus interpreted to be in an amorphous state likely constituted of various poly-N arrangements. This is possibly due to the fact that in the pressure range between 188 and 263 GPa, eight single-bonded phases of nitrogen are predicted by *ab initio* calculation with enthalpy differences of less than 50 meV [6]. As a result, it constitutes a multivalley degenerate enthalpy landscape that could promote an amorphous state. Finally, increasing the pressure to 244 GPa and laser heating the sample to 3300 K resulted in a drastic rise in transparency and the appearance of diffraction peaks, as illustrated in Fig. 1. In the angle-resolved x-ray diffraction patterns, there is a significant overlapping of peaks between the novel poly-N phase and the Re gasket: although the x-ray spot was 3 μm at half-width, the tail of the x-ray beam extended to the Re at the edge of the 12 μm diameter N sample. Fortunately, because the synthesized nitrogen sample has a multigrain texture, the diffraction peaks from the novel poly-N phase could be well identified on the image plate (see Fig. 2). These diffraction spots were followed down to 176 GPa. The evolution of the 2θ diffraction peaks position versus pressure is given in the Supplemental Material [19].

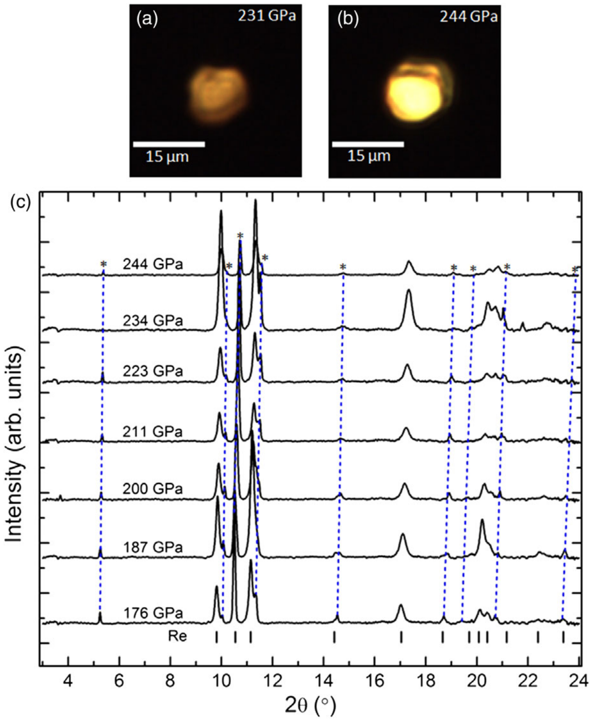

FIG. 1. Microphotographs of the nitrogen samples after laser heating at (a) 231 GPa and (b) 244 GPa, under transmitted light. (c) Integrated x-ray diffraction patterns collected with an x-ray wavelength of $\lambda = 0.3738$ Å. The integrated diffraction patterns were obtained after laser heating the sample to 3300 K at 244 GPa. The transformed sample thus obtained was then probed under decompression down to 176 GPa. The Re peaks are marked at 176 GPa by black tick lines. The blue dashed lines indicate the nine diffraction lines of HLP-N, also identified at 244 GPa by asterisks, which could be followed with pressure. The integrated diffraction patterns are shifted along the y axis for clarity.

The newly observed diffraction peaks did not match any of the three previously synthesized polynitrogen phases: cg-N, $Pba2$, and $C2/c$ [13,14]. Moreover, a comparison of the integrated diffraction patterns to the theoretically predicted diamondoid N_{10} cubic (I-$43m$) structure, expected to be stable above 263 GPa, did not provide a good fit. Yet, another predicted structure with a tetragonal ($P4_2bc$) lattice proved to well explain all of the new diffraction lines [6]. This was confirmed by a Le Bail refinement, performed on a diffractogram recorded at 187 GPa. The following lattice parameters were obtained: $a = 4.261(1)$ Å and $c = 8.120(1)$ Å ($V = 147.43$ Å^3). Because of the preferred orientation of the synthesized phase, mainly the peaks along the ($h0l$) direction could be discerned. A total of nine diffraction peaks could be followed from 244 GPa down to 176 GPa, as shown in Fig. 1; enough for an accurate determination of the tetragonal lattice parameters.

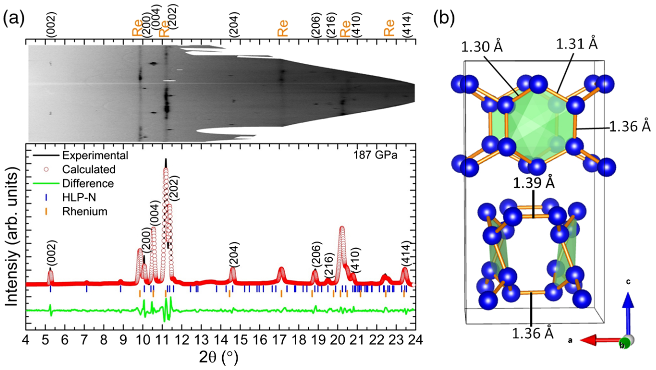

FIG. 2. (a) Le Bail refinement of the integrated x-ray diffraction pattern recorded at 187 GPa after synthesis at 244 GPa and decompression. The (hkl) indexes of the experimentally observed diffraction peaks are marked. Lattice parameters of $a = 4.261(1)$ Å and $c = 8.120(1)$ Å ($V = 147.43$ Å^3) were obtained. The raw x-ray diffraction image, obtained with $\lambda = 0.3738$ Å, is shown above and the diffraction spots of the multigrain HLP-N sample can be discerned from the Re powder lines. (b) Drawing of the $P4_2bc$ crystal structure at 235 GPa, with the five distinct N—N bond lengths marked. For clarity, the inner surface of the N_6 hexagons is filled with a light green plane. The layered nature of the $P4_2bc$ structure is clearly seen.

Structural optimizations within density-functional theory calculations have been performed, as detailed in the Supplemental Material [19], to obtain the $T = 0$ K enthalpy and the compression curve for the four best candidate structures (given in previous theoretical work [6]) of singly bonded nitrogen in the pressure range covered here: cg-N, $Pba2$ (LP-N), $P4_2bc$ (HLP-N), and N_{10}. In agreement with a previous calculation, the tetragonal ($P4_2bc$) lattice contains 32 nitrogen atoms sitting on four distinct $8c$ Wyckoff positions (the parameters are given in Table S2 in the Supplemental Material), each bonded to three nitrogen atoms [6]. As represented in Fig. 2, the N atoms are organized into layers stacked along the c axis and made of distorted N_6 hexagons perpendicular to the a axis and b axis, successively. On account of the layered nature of this new phase composed of N_6 hexagons, it is here called the hexagonal layered polymeric nitrogen (HLP-N). According to the calculations, at 235 GPa the shortest interlayer N-N distance is of 2.02 Å, similar to the shortest intermolecular distance in pure molecular nitrogen at 100 GPa [33]. As identified in Fig. 2(b), within the hexagons there are three distinct N-N distances between 1.30–1.36 Å while bond lengths of 1.36 and 1.38 Å are observed to link the N_6 rings. All of these lengths are characteristic of single-bonded nitrogen atoms, as found in cg-N and in the $Pba2$ phase [13,14]. This also unambiguously confirms the symmetry lowering of the poly-N with pressure, from 3D (cg-N) to 2D ($P4_2bc$).

The single-bonded N-N nature of the synthesized $P4_2bc$ was further confirmed by performing Raman spectroscopy measurements. Twelve distinct vibrational modes were detected (see Fig. 3) among which seven at frequencies between 650 and 1300 cm^{-1}, matching the frequency range of other compounds containing single-bonded nitrogen atoms [34–37]. This includes the main Raman modes of cg-N (750–875 cm^{-1}) and of LP-N (860–1020 cm^{-1} and 1200–1310 cm^{-1}), found between 60 and 150 GPa in the literature [13,14]—and reproduced through our measurements, obtained from 56 to 165 GPa (see Supplemental Material [19]). It should be noted that at the maximum pressure of 244 GPa, the sample presents a strong fluorescence when irradiated with either the 488 or 647.1 nm wavelengths and only the three most intense Raman modes could barely be observed. This fluorescence significantly decreases during sample decompression, allowing the detection of lower intensity Raman peaks. Between 244 and 176 GPa, the sample was characterized by x-ray diffraction only. As seen in Fig. 3 and the Supplemental Material, Fig. S3 [19], the continuity of the Raman mode frequencies versus pressure indicate that the HLP-N phase is metastable upon pressure release at least down to 66 GPa, where the pressure release was stopped due to a diamond anvil failure.

To provide further evidence of the synthesis of the HLP-N compound with a $P4_2bc$ structure, the Raman tensors for the different vibration modes at the Γ point were calculated at five different pressures using density-functional perturbation theory, at the linear and nonlinear levels, as implemented in ABINIT (see details in the Supplemental Material [19]) [38]. The Raman intensities were deduced, for each mode, from the Raman tensors [39]. In total, 81 modes with nonzero Raman tensors (58 when accounting for the modes' degeneracy) were obtained and found at frequencies between 230 and 1425 cm^{-1} at 80 GPa. The comparison between the most intense theoretical modes and the experimental ones is shown in Fig. 3. The resemblance of the experimentally detected modes—and in particular the main ones found between 800 and 1200 cm^{-1}—to the calculated ones, both with regards to their relative intensities as well as their frequencies, is striking. When also taking into consideration the calculated modes of lower intensity (see Fig. S5 in the Supplemental Material [19]), all experimental modes of frequencies below 800 cm^{-1} are explained. Of course, the calculated modes just

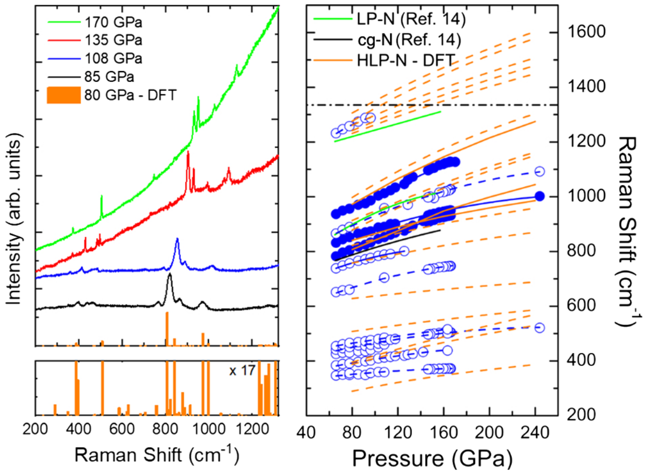

FIG. 3. (Left) Experimental Raman spectra of HLP-N. The spectra obtained during sample decompression from 170 to 85 GPa have been offset for clarity. At 244 GPa, the sample fluorescence only permitted the detection of the three most intense modes. Fluorescence of the sample decreased upon pressure release. At the bottom of the graph are represented the calculated Raman spectrum for the HLP-N ($P4_2bc$) structure at 80 GPa, displaying a clear match with the experimentally measured peaks. The panel below provides an enlargement of the calculated Raman modes, allowing for the weaker ones to be seen. Metastability of HLP-N could be followed down to 66 GPa (see Fig. S3). (Right) Evolution of the Raman mode frequencies of the HLP-N ($P4_2bc$) solid with pressure. The blue symbols and lines represent the experimental data, with the most intense modes identified by full lines and full circles. Selected based on their intensity, 18 modes belonging to the calculated HLP-N $P4_2bc$ structure are drawn (orange), with the three highest intensity ones distinguished by full lines. The full green and black lines correspond to the LP-N and cg-N Raman modes, respectively, as reported in Ref. [14]. The horizontal dashed line at 1330 cm^{-1} marks the beginning of diamond's intense Raman mode which prevents the observation of the calculated HLP-N solid vibrational mode at higher frequencies.

above 1330 cm^{-1} could not be observed due to the much more intense Raman mode of the diamond anvils. The computed intensities were calculated based on the approximation that the sample is a perfect powder (see Supplemental Material). As illustrated in Fig. 2, the measured sample is shown to deviate from a perfect powder and thus provides an explanation from the small differences between the calculated and the experimental intensities.

The $T = 0$ K compression curves calculated for the cg-N, $Pba2$, $P4_2bc$, and N_{10} structures are plotted as dashed lines in Fig. 4(a). The packing efficiency is seen to increase along the sequence cg-N, $Pba2$, $P4_2bc$, N_{10}, that is by going from a 3D to 2D to 3D superatom N-singly bonded arrangements [6]. The compression curves of $Pba2$ and $P4_2bc$ are very near, underlining the similarity between these two layered structures constituted of linked chains of N quasihexagons. The present experimental data for the $P4_2bc$ structure are in good agreement with calculations, with a slightly higher volume at a given pressure that could partly be explained by the thermal expansion of experiment ($T = 300$ K). The experimental data for cg-N (obtained from the literature [14]) are also in good agreement with the calculations. However, the experimental volumes measured for the $Pba2$ structure, reported in Ref. [14], are much lower than the calculations. That is an indication that the $Pba2$ structure assignment for the so-called LP-N phase reported in Ref. [14] might not be correct.

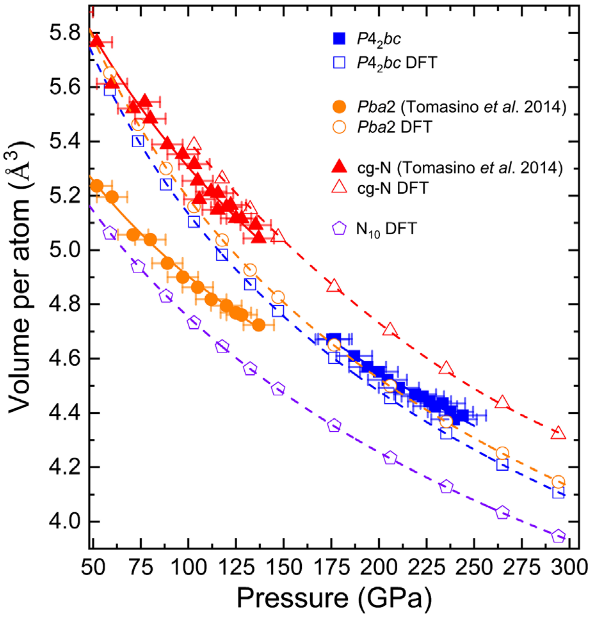

FIG. 4. Comparison between calculation and experimental data. (a) Evolution of the compression curve of various polynitrogen solids. The dashed lines indicate the present $T = 0$ K calculation for the cg-N, $Pba2$, $P4_2bc$, and N_{10} structures, respectively, as red, orange, blue, and purple. The full symbols are the experimental data from ref. [14], for cg-N and $Pba2$, as well as the present data for $P4_2bc$.

Calculation of the $T = 0$ K enthalpy-pressure relations for the most stable structures around 250 GPa are plotted in Fig. S11 of the Supplemental Material [19]. Because of the very small enthalpy differences between these various structures, the structural optimization and the convergence of the calculation were pushed below 1 meV/atom (see Supplemental Material [19]). At 244 GPa, the enthalpy of $P4_2bc$ is 11 meV greater than that of $Pba2$, in very good agreement with the previous calculations [6]. Adding the thermal and dispersive interaction contributions still do not make the $P4_2bc$ structure the most stable phase. The thermal (vibrational) contribution, calculated at the temperature of the synthesis (3300 K), was estimated in the harmonic approximation and obtained by calculating the phonon band structure of the $P4_2bc$ and $Pba2$ arrangements at 244 and 300 GPa. Both structures are dynamically stable with no imaginary mode. The thermal contribution to the Gibbs free energy difference at 244 GPa (300 GPa), essentially given by the entropy term, only increases (lowers) the difference between $P4_2bc$ and $Pba2$ by 0.7 meV (1 meV) only. The influence of dispersive interactions was also tested by correcting the GGA-PBE functional with the semiempirical scheme of Grimme [40,41]: the enthalpy difference between $P4_2bc$ and $Pba2$ is only reduced by $\sim$2 meV/atom only, and at 244 GPa, the $Pba2$ structure is still found to be more stable than $P4_2bc$ by $\sim$9 meV/atom. Performing the calculations with a higher degree of approximation, i.e., taking into account the anharmonic terms in the thermal contribution or using another exchange-correlation functional that would bring a perfect agreement with the compression curve, could probably reverse the Gibbs free energy difference between $Pba2$ and $P4_2bc$. However, that is beyond the scope of the present Letter.

In summary, pure nitrogen was investigated up to the most extreme conditions yet reached through its static compression: 244 GPa and 3300 K. The $P4_2bc$ polymeric singly bonded phase was synthesized, as demonstrated by x-ray diffraction measurements and the comparison of its experimental and theoretical Raman modes. It is a layered structure, composed of interconnected chains of N_6 rings, named the HLP-N phase. That is surprising since the $Pba2$ structure is given as being slightly more stable by calculations and was reported in a previous experimental study. On one hand, we show here that the previous assignment of the $Pba2$ structure to LP-N can be questioned. On the other hand, even by taking into account dispersive interactions and thermal contributions, the $Pba2$ phase is still calculated slightly more energetically favorable. That should motivate further calculations that could test anharmonic effects and other exchange-correlation functionals. Moreover, an interesting point that could be explored to explain the synthesis of the HLP-N solid is the comparison of the activation barrier energy for a transformation of amorphous nitrogen towards the HLP-N phase and the LP-N phase. The present observations unambiguously confirm the predicted structural evolution of polymeric nitrogen from a 3D (cg-N) to a 2D layered structure. The next experimental step would be the synthesis of the superatom N_{10} structure but pressures in excess of 300 GPa would have to be reached.

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