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Low-pressure metastable phase of single-bonded polymeric nitrogen from a helical structure motif and first-principles calculations

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Recognition of helical structural motifs in the experimentally observed *cubic gauche* (CG) crystal lattice has led to the discovery of a single-bonded nonlayered nitrogen structure that we have named *chaired web* (CW). First-principles density functional theory calculations reveal that CW, which was originally identified at high pressures, possesses metastability at ambient conditions as well. The metastability is demonstrated by both high-quality phonon dispersion calculations and finite-temperature first-principles molecular dynamics simulations. In addition, the CW phase is thermodynamically more stable than the CG phase in the ambient pressure regime.

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At extremely high pressures the triple-bonded form of molecular nitrogen, which is the most stable form of nitrogen at low pressures, transforms into an extended polymeric structure. In the recent literature, this form of nitrogen, known as polymeric nitrogen, has received considerable attention for its potential use as a high-energy material. The existence of polymeric phases of nitrogen under high pressure was first speculated in a number of theoretical articles starting in the 1980s.[1,2] In a groundbreaking work, Mailhiot *et al.*[3] postulated a phase of polymeric nitrogen, which they named *cubic gauche* (CG), whose structure had no known analogs in nature. Based on first-principles calculations, the authors predicted this structure to be the most favorable form of nitrogen above ~20 GPa. The first syntheses of polymeric nitrogen were reported in 2000 (Refs. 4 and 5) with subsequent investigations pointing to an amorphous phase having been produced. In 2004, a crystalline form of nonmolecular polymeric nitrogen was synthesized via high pressure (110 GPa) and temperature (2000 K).[6] Remarkably, this phase was determined to have the computationally postulated CG structure.

Although CG has been heralded theoretically as the most favorable form of single-bonded polymeric nitrogen and is currently the only structure to be characterized experimentally, other phases have also been discussed in the literature.[3,7–9] The search for alternatives to the CG phase is motivated by practical considerations. At present, CG has not been stabilized at low pressures and therefore the lifetime of CG at ambient conditions is not known. For a polymeric nitrogen phase to be used in practice as a high-energy density material, it should have a long lifetime of metastability at ambient pressures, have high-energy content, and be able to be made efficiently in bulk quantities. At this point it is not clear that CG possesses all of these properties and, therefore, alternative polymeric nitrogen phases with some or all of the aforementioned properties are of great practical interest. In addition, there could be other physical conditions, apart from high pressure and temperature, leading to the formation of polymeric nitrogen under which conditions new allotropes could manifest themselves. For example, in a recent experiment combining photoexcitation with traditional high-pressure diamond anvil techniques, potentially new polymeric nitrogen phases were observed at 170 GPa.[10]

Several strategies have been taken in proposing possible structures of polymeric nitrogen. Initially, nature served as inspiration.[1] Structural analogs of naturally occurring forms of elements lying below nitrogen in the periodic table were studied—namely, the black phosphorous (BP) and α-arsenic ($A7$) structures. The CG structure first proposed by Mailhiot *et al.*,[3] was "rationally designed" with the notion that the dihedral angle in a N-N single bond energetically prefers a *gauche* conformation. The CG structure maximizes this, such that every N-N bond is in a *gauche* conformation, resulting in a very thermodynamically stable structure across a wide range of pressures. More recently, new structures have been "discovered" from first-principles molecular dynamics calculations in what could be described as computational experiments.[7–9] In these studies, high-pressure and high-temperature conditions similar to those used to synthesize the materials in the laboratory are simulated with the hope that new structures will evolve. One purely single-bonded phase and two unsaturated chainlike phases were found with this approach. One of the chainlike phases, which we will term the zigzag chain (zzCH), was deemed to be particularly promising since it was thermodynamically competitive with CG at low pressure and even lower in enthalpy at ambient pressures.[7] Recently, we have devised a systematic method[11] for generating purely single-bonded polynitrogen structures from distortions of a simple cubic reference structure. From this approach, eight new structures were found that were computationally confirmed to be mechanically stable at pressures less than 100 GPa, including two structures that were characterized as metastable at zero pressure. Nonetheless, at low pressures, CG was still found to be the most enthalpically favorable single-bonded structure.

In this Rapid Communication we present a single-bonded phase of polymeric nitrogen that was rationally developed by recognizing a helical structural motif in CG and other single-bonded phases. This phase, which we have termed *chaired web* (CW), is calculated to be slightly more thermodynamically stable than CG at ambient pressure and has been rigorously determined to be metastable based on first-principles calculations. Thus, except for the fact that it has not been experimentally observed, this structure may be considered as similar in significance as CG. Herein, we will show that helical chains are a natural structural theme in polymeric nitrogen; we demonstrate how it was used to find the CW structure and elaborate upon the computed properties of this new phase.

The results presented here were obtained by first-principles density functional theory calculations with the Perdew-Burke-Ernzerhof (PBE)[12] exchange-correlation functional. The SIESTA (Ref. 13) package was used for most of the exploratory simulations, such as preliminary optimization of structures, and molecular dynamics simulations, while VASP (Ref. 14) was used to calculate the final phase diagram, phonon dispersion, and band structure. For the SIESTA calculations, the Troullier-Martins[15] norm-conserving pseudopotential with a nitrogen reference configuration of $[\mathrm{He}]2s^2 2p^3$ and a cutoff radius of 0.98 Å was utilized. A custom numerical "double-ζ with polarization" SIESTA-type basis set[16] was developed for the calculations. A 10-Å cutoff was employed for the k-point sampling. The calculations performed with VASP were based on the projector augmented wave (PAW) method of Blöchl[17] where a 39-Ry plane-wave cutoff and Brillouin-zone integration with $12\times12\times12$ Monkhorst-Pack grid were used. In both programs a variable-cell-shape conjugate gradient method under constant pressure was used for the minimization of the geometries and molecular dynamics was performed within the Nosé-Parinello-Raman scheme.

Ab initio calculations on small molecules of the type R_2-N-N-R_2 demonstrated that the most favorable dihedral angle is the so-called "gauche" dihedral—i.e., around 120°—due to the effect of hyperconjugation and mutual repulsion of nitrogen's lone electron pairs.[3] Mailhiot, Yang, and McMahan postulated the structure of CG based on the idea of maximizing the number of gauche dihedral angles within a single-bonded nitrogen network and named it accordingly.[3] If one constructs a chain of atoms where all dihedral angles are *gauche*, this results in the formation of right- or left-handed helices, depending on whether a dihedral of $\sim+120°$ or $-120°$ is applied. Indeed, within the CG structure, helices that have four and eight atoms per turn can be identified along the [100] direction and threefold helices can be located along the [110] direction. Figure 1(D) highlights the eightfold helices in CG.

Pure helices are also observed in some high-pressure phases of group-16 elements, such as sulfur, selenium, and tellurium[18–20] as well as in scandium.[21] Unlike the group-16 elements, nitrogen cannot form stable helices on its own. In order to acquire stability a single helical chain of nitrogen atoms has to have its valence saturated (form three single bonds). If the valence is not saturated, then partial double bonds will form and the chain will flatten out to either a *cis-trans* or *zigzag* chain. In the latter case the energy lowers by 0.5 eV per atom. The reverse tendency also holds—namely, *cis-trans* or *zigzag* chains acquire helicity once capped due to the above mentioned "gauche effect" and the energy is lowered by 0.6 eV per capped atom. It is interesting to note that in both cases the lowering of energy is achieved by changes in the local hybridization (from sp^3 to sp^2 and vice versa), symmetry breaking, and splitting of degeneracy at the Fermi level. These are characteristic of a Peierls deformation. If a pure nitrogen structure is sought, the helices have to be brought close enough to each other in order to create interhelical bonds. The geometry of CG could be thought of as such a structure where interlinked nitrogen helices form a single-bonded network as illustrated in Fig. 1(D).

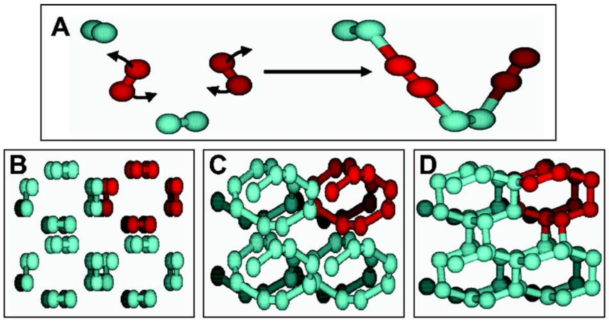

FIG. 1. (Color online) (A) Flipping or "inverting" two [highlighted in red (dark gray)] out of four N_2 molecules in the primitive unit cell of the molecular ζ phase (left) results in an eightfold helical chain structure (right). (B) ζ phase, (C) "inverted" ζ phase, and (D) CG. For (B), (C), and (D) a $2\times2\times2$ supercell is shown with one helical chain highlighted in red (dark gray).

The base helical structure of CG can be formed from what has been proposed to be the molecular ζ phase, which itself is considered to be the immediate molecular precursor[22] of CG during its synthesis. Helices can be formed by changing the alignment of two out of the four N_2 molecules within the primitive unit cell of the ζ structure. The necessary rotation about the two molecule's center of mass as to "invert" their orientation is shown in Fig. 1(A). Using this inverted ζ structure [Fig. 1(B)] as a starting geometry for a first-principles calculation, eightfold helical chains form after only a few optimization steps as depicted in Fig. 1(C). Further optimization at high pressure leads to the formation of the single-bonded CG phase [Fig. 1(D)]. In a similar manner the geometry optimization of properly arranged fourfold and threefold helical chains also result in the formation of CG.

It is natural to propose that certain arrangements of the helical nitrogen chains could form the basis of other polynitrogen structures. To achieve a structure where all nitrogen atoms are three-coordinates, bonds between adjacent chains must be made because the nitrogen atoms are only two-coordinate in the pure helical chains. Different arrangements of threefold, fourfold, etc., helices or of their combinations could lead to alternative structures. For example, a slight rearrangement of the threefold helices within CG results in a structure that has recently been proposed as a new polynitrogen structure.[23] Arrangement and connection of sixfold helical chains as shown in Fig. 2, followed by geometry optimization, produced a stable structure we have called *chaired-web* (CW). Connecting the helical chains together results in the formation of a network of six-member rings that are in the so-called "chair" conformation, as the name given to the structure suggests. Figure 3(A) highlights the six-member rings of the CW.

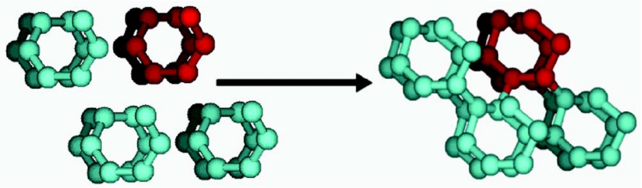

FIG. 2. (Color online) A properly arranged set of sixfold helices (left) forming the single-bonded CW phase (right).

The structure and symmetry of the new phase is better seen in Fig. 3. If the original helices posses clockwise turns [depicted in Fig. 3(B) in red], then new helices with counterclockwise turns [depicted in Fig. 3(B) in green] are naturally formed in between the original helices due to the interhelical bonds. The aforementioned six-membered rings are formed in the voids between the helices as shown in white in Fig. 3(B). These voids accommodate the nitrogen lone pairs. All of the six-member rings are in the so-called chair conformation. The interplay of helical chain and six-ring structural motifs in CW is reminiscent of *cis-trans* chain and six-membered ring motifs interplay in the layered phases BP, *A*7, and LB.[9] Additionally, we note that the structure of CW can be obtained by applying our systematic method for generating purely single-bonded polymeric nitrogen.[11] However, the eight-atom simple cubic reference cell first demonstrated[11] would not be large enough to generate CW. Rather a significantly expanded 48-atom (or larger) simple cubic reference structure would have to be employed.

The primitive unit cell of CW is rhombohedral. At an intermediate pressure of 28 GPa the unit cell vector length is 3.5 Å with an angle measuring 99.172° and the corresponding symmetry group is $R\bar{3}m$. The six equivalent atomic positions could be recovered from (0.8756, 0.8756, 0.3206) in fractional coordinates by the use of symmetry. There are two types of interatomic distances in the crystal lattice, a shorter N-N distance within a given six-member ring and slightly longer N-N distance between two adjacent six-member rings. At 28 GPa these distances are 1.36 Å and 1.45 Å, respectively. There is a 2:1:0 ratio of *gauche*-, *trans*-, and *cis*-dihedral angles in the crystal lattice. Band structure calculations show that CW is an insulator at low pressure with a calculated band gap of ~5 eV. A simulated x-ray diffraction spectrum is provided in the supplemental material.[24] The phase diagram shown in Fig. 4 demonstrates how close CW is to CG in terms of enthalpy. At zero pressure the enthalpy favors CW over CG by approximately 20 meV. The temperature-dependant free-energy and zero-point energy corrections within the harmonic approximation[24] have been evaluated at zero pressure. The zero-point energy correction favors CG over CW by 54 meV, thus reversing the energy order of the two phases at zero temperature. With the rise in temperature there is a crossover of the two free-energy dependences around 200 K. At ambient temperature the new CW phase is thermodynamically more stable than the CG phase with 83 meV in free energy.

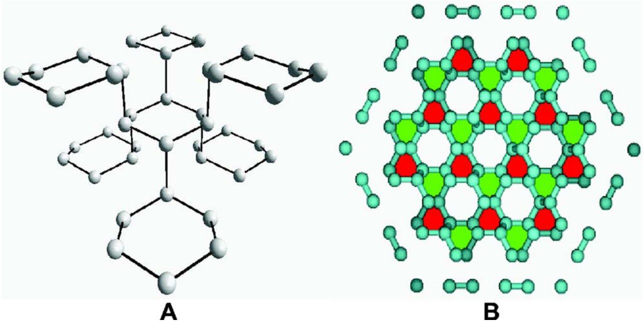

FIG. 3. (Color online) Lattice structure of CW: (A) Perspective view, (B) a view along [111]. Left- [red (dark gray)] and right- [green (light gray)] oriented sixfold helices with six rings (white) lying between them within CW phase (3×3×3 supercell).

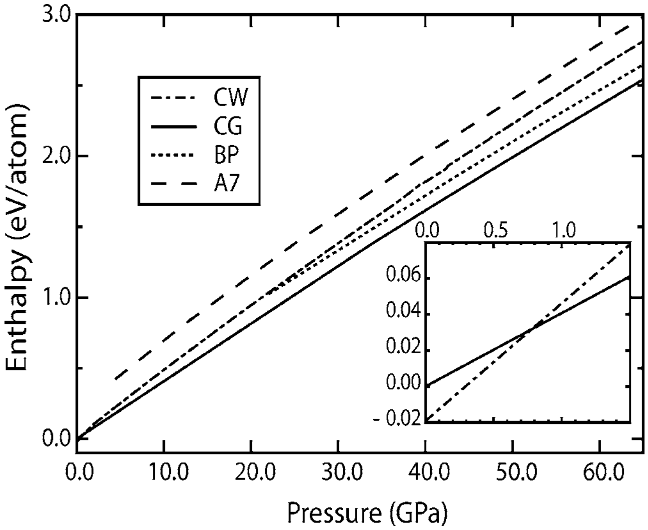

FIG. 4. Relative enthalpy versus pressure phase diagram of CW, CG, BP, and *A*7. Enthalpy is relative to CG at 0 pressure. The caption in the lower right corner enlarges the low-pressure region.

The results of high-quality phonon dispersion calculations are shown in Fig. 5. The lack of negative modes establishes the structural metastability of the CW phase at very low pressures. Although the phonon-dispersion curve of Fig. 5 is to be considered a theoretically rigorous verification of CWs metastability, we have also performed three additional tests to probe the energy barrier of decomposition: (i) a random displacement test in which the structure is optimized after the

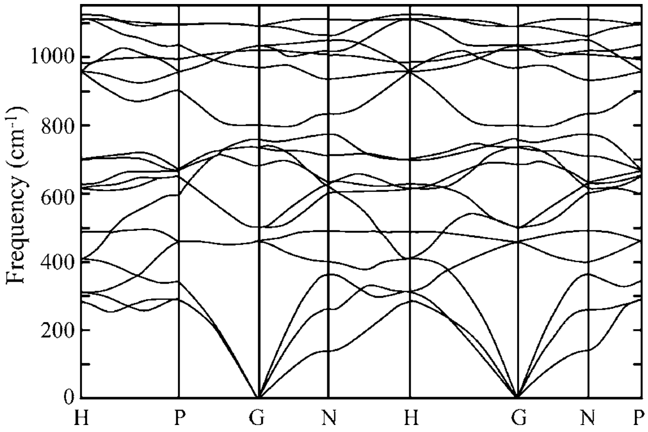

FIG. 5. Phonon dispersion of the CW phase at 0 GPa.

positions of atoms are randomly displaced by 5% of their interatomic distance, (ii) first-principles molecular dynamics (FPMD) test at 0 GPa, 300 K for 10 ps, and (iii) a hybrid test in which ten random snapshots of the initially equilibrated system are taken, the positions and velocities are randomly perturbed, and the system is further a subject to FPMD at 0 GPa, 300 K for an additional 4 ps. A rigorous study of CWs metastability lifetime is substantially more challenging, but the tests indicate that the lifetime of CW may be of practical interest.

The structure of CW is, as are other purely single-bonded polymeric nitrogen phases, governed to a large extent by the repulsion of the lone pairs. In CW the inherent stability of the initial *gauche* helices and the newly formed helices of reverse handedness is offset by the repulsion of the lone pairs from neighboring helices. Importantly, in CW the lone pairs point into large void spaces, thereby reducing the repulsion. A figure depicting this is given in the supplemental material.[24] At high pressure the large voids are thermodynamically unfavorable because of the associated enthalpic penalty. On the other hand, at low pressure, the balance between these two contradictory influences of the lone pairs is such that CW is more stable than CG at ambient pressures.

In looking for a possible precursor of CW one has to note that the traditional understanding of N_2 phase diagram was recently questioned and preliminary results suggest the need for its extension and/or revision.[25] In particular, Sanloup *et al.*[26] found a molecular phase characterized by a configuration of three nitrogen molecules nearly forming a six-member ring. One could speculate that CW could be formed from such a phase under appropriately engineered physical conditions.

In conclusion, we report a metastable phase of single-bonded polymeric nitrogen by first-principles simulations. A guiding principle in identifying the geometry of CW is the use of helical chains as a structural pattern, complementary to both are previous use of *cis-trans* and *zigzag* chains as structural patterns and our systematic combinatorial search method based on Peierls-like deformations of simple cubic lattices. The metastability of CW is demonstrated by high-quality phonon-dispersion calulations and finite-temperature Parrinello-Rahman molecular dynamics. An enthalpy versus pressure diagram compares CW with other known phases of polymeric nitrogen: the experimentally observed CG and computationally studied layered BP and *A*7 phases. This comparison reveals that CW is, to date, the only known metastable phase of single-bonded polymeric nitrogen that is thermodynamically competitive with CG in the low-pressure region.

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