Stable All-Nitrogen Metallic Salt at Terapascal Pressures

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The phase diagram and equation of state of dense nitrogen are of interest in understanding the fundamental physics and chemistry under extreme conditions, including planetary processes, and in discovering new materials. We predict several stable phases of nitrogen at multi-TPa pressures, including a $P4/nbm$ structure consisting of partially charged $N_2^{\delta+}$ pairs and $N_5^{\delta-}$ tetrahedra, which is stable in the range 2.5–6.8 TPa. This is followed by a modulated layered structure between 6.8 and 12.6 TPa, which also exhibits a significant charge transfer. The $P4/nbm$ metallic nitrogen salt and the modulated structure are stable at high pressures and temperatures, and they exhibit strongly ionic features and charge density distortions, which is unexpected in an element under such extreme conditions and could represent a new class of nitrogen materials. The P-T phase diagram of nitrogen at TPa pressures is investigated using quasiharmonic phonon calculations and *ab initio* molecular dynamics simulations.

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The polymerization of molecular nitrogen under pressure has been very actively researched over the past two decades and has stimulated many experimental [1–12] and theoretical [13–31] investigations. Density functional theory studies suggested that the dissociation of nitrogen could occur at high pressures which are, nevertheless, attainable in diamond anvil cell experiments. In a ground-breaking paper, Mailhiot *et al.* [16] predicted the polymerization of nitrogen molecules under pressure, leading to the formation of the "cubic *gauche*" (cg) framework structure (space group $I2_13$). After considerable efforts [1,2], cg nitrogen was finally synthesized by Eremets *et al.* [5], a decade after its prediction. Novel techniques must be developed if cg-N is to be recovered to ambient pressure [5], which could lead to the synthesis of polymeric nitrogen [5] or high-N content salts [32]. Such materials are expected to be excellent candidates as high-energy-density materials.

The $N{\equiv}N$ triple bond is one of the strongest known, and breaking it requires surmounting a substantial energetic barrier. However, at high temperatures the triple bond breaks at pressures above about 110 GPa [5], a much lower pressure than predicted for the single bond in H_2 [33] and the double bond in O_2, which is predicted to survive up to about 1.9 TPa [34,35]. Once the N≡N triple bond is broken, a wide variety of structures can be adopted, similar to phosphorus and arsenic.

After extensive searches for high-pressure nitrogen structures, the sequence of low-temperature phase transitions cg → $Pba2$ → $P2_12_12_1$ appeared to be accepted [28,29]. That view was challenged recently, when a cagelike diamondoid "N10" structure (space group $I\bar{4}3m$) was found to be more stable than any other candidate above 263 GPa [31]. Recently, the melting behavior of nitrogen and phases beyond cg-N have also been investigated [10–12,30].

Recently, dynamical shock wave [36–38] and ramped compression experiments [39–41] have increasingly been used to investigate materials at TPa pressures. Even more extreme conditions are attainable today in laser ignition experiments [42] and laser-induced microexplosions [43]. Experimental determinations of structures at TPa pressures will soon be possible [41], and experiments aimed at compressing nitrogen to TPa pressures are ongoing [44]. However, there is very little knowledge of the structures and properties of nitrogen under these conditions, and therefore theoretical predictions are particularly important [34,45–48]. Understanding the energetics of elements is crucial before one can understand the energetics of the compounds they might form.

Although an increase in coordination number with pressure seems physically reasonable, it is by no means universal. Aluminum, for example, is expected to adopt more open structures at TPa pressures as the valence electrons move away from the ions in the formation of "electride structures" [47]. Well-packed structures are strongly disfavored in oxygen up to at least 25 TPa [34], which is well beyond dissociation. The coordination number of nitrogen has not been determined beyond 800 GPa, at which pressure the insulating N10 ($I\bar{4}3m$) phase is stable.

We have used *ab initio* random structure searching (AIRSS) [49,50] and density functional theory methods to find candidate structures of nitrogen up to multi-TPa pressures. Details of the searches are provided in the Supplemental Material [51]. These searches have enabled

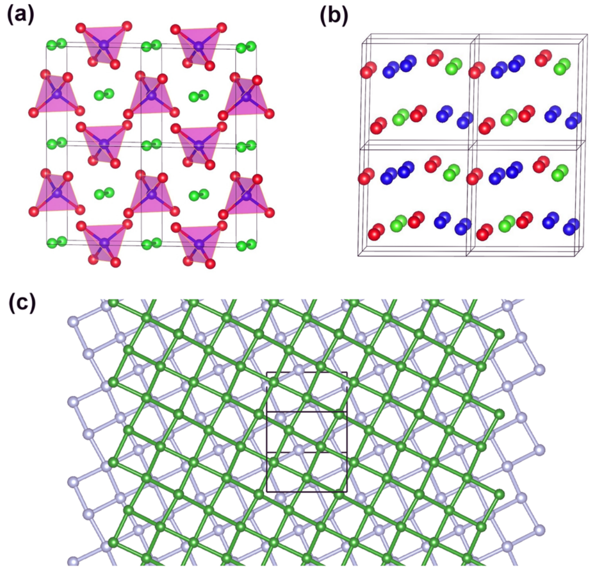

FIG. 1 (color online). Crystal structures of the newly predicted nitrogen phases. (a) $P4/nbm$, (b) $P2_1$, (c) A supercell of $P2_1$ viewed along the a axis. The colored spheres in (a) and (b) represent atoms with different charge environments, as described in the text. Atoms in different layers in (c) have been shown with different colors.

us to identify a number of novel candidate structures. Four of them are thermodynamically stable within certain pressure ranges, namely, $P4/nbm$ ($Z = 14$), where Z is the number of atoms in the unit cell, $P2_1$ ($Z = 10$), $R\bar{3}m$ ($Z = 3$), and $I4_1/amd$ ($Z = 4$). The most important structures are shown in Fig. 1 and defined in Table I. Most interestingly, the tetragonal $P4/nbm$ structure is characterized by the presence of N_2 pairs and N_5 tetrahedra. At 2.5 TPa, the N-N bond length within the N_5 tetrahedra is 1.13 Å, and the shortest distance between the corners of the tetrahedra and N_2 dimers is 1.26 Å. The N-N bond length within the dimer of about 1.17 Å is significantly shorter than the N-N separation between adjacent dimers (about 1.29 Å), implying that the dimers are separated.

The unique structure of the $P4/nbm$ phase led us to perform a Bader charge transfer analysis [52]. As summarized in Table I, we found that the N_5 tetrahedra are negatively charged ($-0.37|e|$) and serve as anions, while the positively charged N_2 dimers ($+0.37|e|$) act as cations. The charge transfers depends on the precise definition of the atomic charges, but the computed charges are substantial, and the overall picture is independent of their definition. We therefore suggest that the $P4/nbm$ structure resembles an all-nitrogen salt.

Our best candidate structure beyond 6.8 TPa, of symmetry $P2_1$ with 10 atoms in the unit cell, also shows a very strong charge transfer. The computed Bader charges range between -0.20 and $+0.35$ $|e|$. This structure can be viewed as two distorted and buckled square layers, rotated with respect to one another by about arctan $\frac{3}{4}$. Similar energetically competitive structures, such as the $Fdd2$ structure, can be formed with different rotation angles. It is likely that the most stable structure at these pressures is an incommensurate charge density wave (CDW) phase. Nevertheless, even after additional directed searches as described in the Supplemental Material [51], the 10-atom $P2_1$ phase remains the best candidate. The appearance of strong charge transfer effects in an element at such high pressures is most unexpected, as the resulting Coulomb energy is substantial.

At lower pressures, we found a $Cmca$ structure similar to "black phosphorus" to be stable within a narrow pressure range. As depicted in the Supplemental Material [51], the $Cmca$ structure consists of threefold-coordinated nitrogen atoms and has zigzag layers, with a shortest N-N distance of about 1.15 Å at 2.5 TPa, which is much shorter than the N-N separation between the layers of about 1.56 Å. Layered structures also appear in the high-pressure phases of other small molecules of first row atoms, e.g., CO [53] and CO_2 [54].

As can be seen in the enthalpy-pressure relations of Fig. 2, solid nitrogen undergoes a series of structural phase transitions beyond the previously known polymeric

TABLE I. Structures and Bader charges (Q_B) of the newly predicted stable nitrogen phases.

Structures	P (TPa)	Lattice parameters (Å)	Atomic positions		Q_B ($\|e\|$)
$Cmca$	2.5	$a = 2.090$, $b = 3.041$, $c = 2.617$	8f	(0.0, 0.3966, 0.8157)	0
$P4/nbm$	2.5	$a = 3.424$, $c = 2.466$	2d	(0.0, 0.5, 0.5)	−0.07
			4g	(0.0, 0.0, 0.7376)	0.18
			8m	(0.1808, 0.6808, 0.7879)	−0.07
$P2_1$	8.0	$a = 2.579$, $b = 2.396$, $c = 2.390$ $\beta = 62.903°$	2a	(0.7889, 0.9079, 0.0325)	0.03
			2a	(0.2912, 0.2331, 0.5345)	0.01
			2a	(0.1858, 0.6314, 0.3824)	−0.20
			2a	(0.2487, 0.8206, 0.7525)	0.35
			2a	(0.6866, 0.5078, 0.8789)	−0.19
$R\bar{3}m$	12	$a = 1.613$, $c = 1.468$	3b	(0.0, 0.0, 0.5)	0
$I4_1/amd$	30	$a = 0.890$, $c = 3.452$	4a	(0.0, 0.25, 0.875)	0

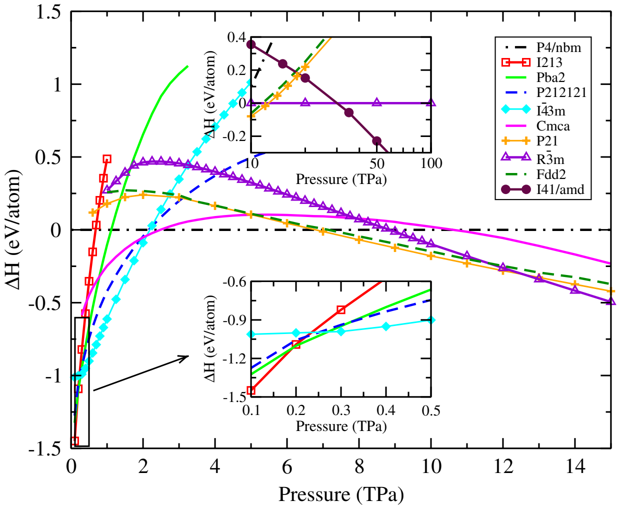

FIG. 2 (color online). Enthalpy-pressure relation for N. The values in the main figure are relative to the enthalpy of $P4/nbm$. The upper inset shows the enthalpies relative to $R\bar{3}m$ at very high pressures. The lower inset shows the enthalpies at low pressures relative to $P4/nbm$.

phases: $I\bar{4}3m \xrightarrow{2.1\ \mathrm{TPa}} Cmca \xrightarrow{2.5\ \mathrm{TPa}} P4/nbm \xrightarrow{6.8\ \mathrm{TPa}} P2_1 \xrightarrow{12.6\ \mathrm{TPa}} R\bar{3}m \xrightarrow{30\ \mathrm{TPa}} I4_1/amd$. The partially ionic $P4/nbm$ phase is stable over a wide pressure range, but compression to about 6.8 TPa leads to the layered $P2_1$ structure. The $P2_1$ structure is the most favorable phase in the range 6.8–12.6 TPa, whereupon it transforms into a sixfold-coordinated hexagonal $R\bar{3}m$ phase. As shown within the inset to Fig. 2, nitrogen forms a $I4_1/amd$ structure similar to Cs-IV [55] at about 30 TPa.

We have established the dynamical stability of the proposed structures by computing their phonon spectra over a wide range of pressures. A selection of phonon spectra is shown in the Supplemental Material [51]. The phonon dispersion relation of $P4/nbm$ shows steep acoustic branches together with fairly flat optical modes. This supports the view that $P4/nbm$ is formed of "units;" the N-N vibrons as well as the breathing mode of the tetrahedra are essentially dispersionless, and are well screened by the electronic cloud. One might expect $P2_1$ to show two relatively soft modes corresponding to a shearing of layers but, in fact, while one of them drops to a very low frequency of 187 cm^{-1} at Γ, the other has a much higher frequency of about 1210 cm^{-1}. This difference in frequency arises from the alignment of shear directions with respect to the ripples in the layers.

We have extended our calculations to include nuclear motion effects so that we can investigate their key role in high-temperature dynamical compression experiments. At low temperatures and pressures $P < 8$ TPa we have calculated the P-T phase diagram within the quasiharmonic approximation (QHA). We have also investigated higher temperatures using *ab initio* molecular dynamics, and have calculated a rough melting curve using the Z method [56] Although the Z method somewhat overestimates melting temperatures, it is a straightforward scheme, and provides an estimated upper bound for the melting temperature, T_m. Our calculated melting temperature could be compared with an experimental Hugoniot. Our results suggest a noticeable increase in T_m with pressure, perhaps monotonic. The melting temperature is about 4700 K for N10 ($I\bar{4}3m$) at 400 GPa, and is as high as 8700 K at 8 TPa for $P2_1$, which is comparable to carbon under similar conditions [57]. The phase diagram of Fig. 3 is generated from a synthesis of our melting data and QHA vibrational results.

The inclusion of vibrational effects reduces the region of stability of $Cmca$ to a small wedge in Fig. 3 and, even in that region, $Cmca$ is never the most stable phase by more than 2 meV/atom. Because the candidate structures have very different characters, their respective vibrational energies differ considerably. As a consequence, vibrational effects make noticeable changes to the transition pressures even at 0 K where, for example, the pressure for the $P4/nbm \rightarrow P2_1$ transition is reduced by 0.5 TPa. The N10 ($I\bar{4}3m$) → $P4/nbm$ transition is not affected as much, because their enthalpies cross with a much larger gradient. Finally, our QHA results greatly reduce the possibility of $P2_12_12_1$ being stabilized by temperature.

Our calculations show that the insulating behavior of nitrogen persists to 2.0 TPa, at which the transition to the metallic $Cmca$ and $P4/nbm$ phases occurs. This is a considerably higher pressure than in other light elements such as hydrogen [33], carbon [48], and oxygen (although oxygen is predicted to become insulating at about 1.9 TPa [34]). The projected density of states shows signs of $2s \rightarrow 2p$ charge transfer only above 15 TPa. The electronic band

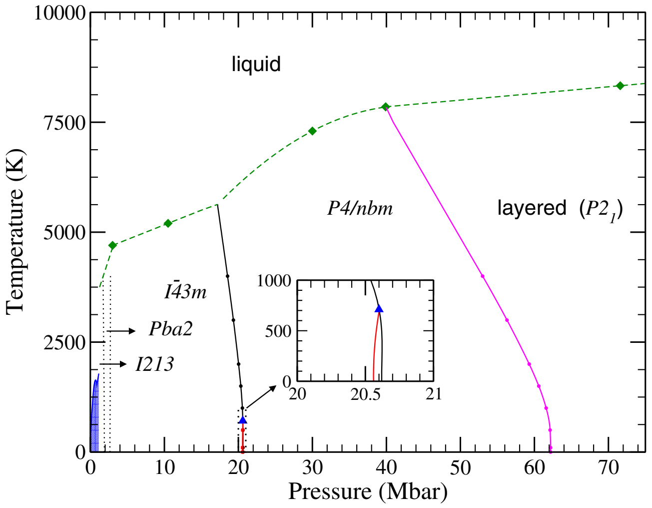

FIG. 3 (color online). Proposed P-T phase diagram of nitrogen. The solid-solid phase boundaries up to 4000 K were computed using the QHA. The melting temperatures were computed using the Z method and *ab initio* molecular dynamics. The shaded blue area on the left corner is the solid molecular N_2 region; the inset depicts the small stability region of $Cmca$.

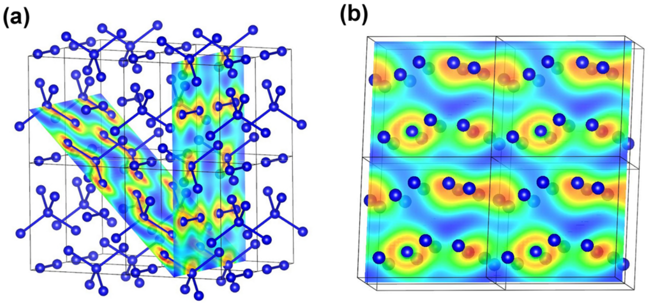

FIG. 4 (color online). Electron densities of polymeric nitrogen. (a) $P4/nbm$ at 2.5 TPa along [100] and [110] directions, (b) $P2_1$ at 8 TPa along [001] directions.

structures and projected density of states of the relevant structures are shown in the Supplemental Material [51].

The formation of N_2 pairs and N_5 tetrahedra in $P4/nbm$ is confirmed by the charge density plot in Fig. 4(b), where the atoms between the tetrahedron center and corners, and between the two atoms within the dimers, form strong covalent bonds. The electron localization function shown in the Supplemental Material [51] provides additional evidence for the formation of tetrahedra and dimers in $P4/nbm$.

The emergence of charged units from an elemental compound has also been observed in γ boron [58]. The pressures of interest in the present study are, however, much larger than those at which γ boron has been observed and, besides, $P4/nbm$ nitrogen is a very different system. The charge transfer in boron satisfies its tendency to form electron deficient icosahedra. Based on the structural richness of phosphorus and arsenic, one might assume that nitrogen could form similarly rich bonding patterns once the triple bond is broken. At 2 TPa, however, packing efficiency is crucial and one would expect structures with high coordination numbers to be formed. In this metallic phase the variation in coordination (or the inhomogeneity of the density of ions) leads to charge transfer from the highly coordinated atoms (“N_2 pairs”) to the lower coordinated ones (“tetrahedra” corners). This charge transfer allows the $P4/nbm$ structure to form a unique metallic all-nitrogen salt. Each atom in the 1D chains perpendicular to the layers of tetrahedra has four long bonds to the corners of the tetrahedra; thus, only one electron is left. The 1D chain with uniform N-N distances is unstable and undergoes a Peierls distortion, similar to that in lithium [59], and N_2 pairs are formed.

Although $P2_1$ also shows a clear charge transfer, the atomic arrangement is completely different from that in $P4/nbm$. This phase is formed by distorted, buckled, and rotated square layers, resembling a CDW. CDWs have been observed previously in chalcogenides under pressure [60]. We believe that nitrogen may actually adopt an incommensurate structure between 6 and 12 TPa. In light of the charge transfer, the buckling of layers could be viewed not only as a symmetry breaking, but also as allowing the positive and negative ions to approach one another and reduce the energy. In addition, while carbon expels charge from the $2s$ levels above 3 TPa [48], eventually forming an electride, the bottom of the valence band of $P2_1$ still has a large $2s$ population. Charge depletion from the $2s$ levels only arises with the transition to the $R\bar{3}m$ phase, at almost 12 TPa. Electride structures are found, for example, in carbon [48] and aluminum [47] at very high pressures, but they do not appear in nitrogen up to at least 100 TPa. While intuition suggests that close-packed structures should be favored under extreme pressures, this is not the case for nitrogen even at 100 TPa where, for example, the face-centered-cubic structure is almost 2 eV per atom higher in enthalpy than $I4_1/amd$.

In conclusion, we have presented a P-T phase diagram for nitrogen using results from first-principles methods. We have used the *ab initio* random structure searching method to investigate N at TPa pressures. We do not find stable close-packed phases below 100 TPa. We have proposed five additional pressure driven phase transitions and two novel phases with unusual behavior. The $P4/nbm$ structure can be seen as a $(N_2{}^{\delta+}N_5{}^{\delta-})_2$ metallic salt, formed from dimers and tetrahedra. The layered $P2_1$ structure also shows strong charge transfer and an undulation resembling a CDW. Our *ab initio* molecular dynamics and Z-method calculations provide a first estimate of the melting curve of nitrogen at TPa pressures.

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